handbook for ANALYTICAL QUALITY CONTROL IN WATER AND WASTEWATER LABORATORIES

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Handbook for Analytical Quality Control in Water and Wastewater Laboratories

National Environmental Research Center

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HANDBOOK FOR ANALYTICAL QUALITY CONTROL IN WATER AND WASTEWATER LABORATORIES

For
U.S. ENVIRONMENTAL PROTECTION AGENCY
Technology Transfer

By
ANALYTICAL QUALITY CONTROL LABORATORY
National Environmental Research Center
Cincinnati, Ohio

June 1972

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ABSTRACT

One of the fundamental responsibilities of management is the establishment of a continuing program to insure the reliability and validity of analytical laboratory and field data gathered in water treatment and wastewater pollution control activities.

This handbook is addressed to laboratory directors, leaders of field investigations, and other personnel who bear responsibility for water and wastewater data. Subject matter of the handbook is concerned primarily with quality control for chemical and physical tests and measurements. Sufficient information is offered to allow the reader to inaugurate, or to reinforce, a program of analytical quality control which will emphasize early recognition, prevention and correction of factors leading to breakdowns in the validity of data.

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Chapter 1

IMPORTANCE OF QUALITY CONTROL

1.1 General

The role of the analytical laboratory is to provide qualitative and quantitative data to be used in decision making. To be valuable, the data must accurately describe the characteristics or the concentration of constituents in the sample submitted to the laboratory. In many cases, an approximate answer or incorrect result is worse than no answer at all, because it will lead to faulty interpretations.

Decisions made using water and wastewater data are far-reaching. Water quality standards are set to establish satisfactory conditions for a given water use. The laboratory data define whether that condition is being met, and whether the water can be used for its intended purpose. If the laboratory results indicate a violation of the standard, action is required on the part of pollution control authorities. With the present emphasis on legal action and social pressures to abate pollution, the analyst should be aware of his responsibility to provide laboratory results that are a reliable description of the sample. Furthermore, the analyst must be aware that his professional competence, the procedures he has used, and the reported values may be used and challenged in court. To satisfactorily meet this challenge, the laboratory data must be backed up by an adequate program to document the proper control and application of all of the factors which affect the final result.

In wastewater analyses, the laboratory data define the treatment plant influent, the status of the steps in the treatment process, and the final load imposed upon the water resources. Decisions on process changes, plant modification, or even the construction of a new facility may be based upon the results of laboratory analyses. The financial implications alone are significant reasons for extreme care in analysis.

Research investigations in water pollution control rest upon a firm base of laboratory data. The final result sought can usually be described in numerical terms. The progress of the research and the alternative pathways available are generally evaluated on the basis of laboratory data. The value of the research effort will depend upon the validity of the laboratory results.

1.2 Quality Control Program

Because of the importance of laboratory analyses and the resulting actions which they produce, a program to insure the reliability of the data is essential. It is recognized that all analysts practice quality control to varying degrees, depending somewhat upon their training, professional pride, and awareness of the importance of the work they are doing. However, under the pressure of daily workload, analytical quality control may be easily neglected. Therefore, an established, routine control program applied to every analytical test is important in assuring the reliability of the final results.

The quality control program in the laboratory has two primary functions. First, the program should monitor the reliability (truth) of the results reported. It should continually provide an answer to "How good (true) are the results submitted?" This phase may be termed "measurement of quality." The second function is the control of quality in order to meet the program requirements for reliability. For example, the processing of spiked samples is the measurement of quality, while the use of analytical grade reagents is a control measure. Just as each analytical method has a rigid protocol, so the quality control associated with that test must also involve definite required steps to monitor and assure that the result is correct. The steps in quality control will vary with the type of analysis. For example, in a titration, standardization of the titrant on a frequent basis is an element of quality control. In an instrumental method, the check-out of instrument response and the calibration of the instrument in concentration units is also a quality control function. Ideally, all of the variables which can affect the final answer should be considered, evaluated, and controlled.

This handbook considers the factors which go into creating an analytical result, and provides recommendations for the control of these factors in order to insure that the best possible answer is obtained. A program based upon these recommendations will give the analyst and his supervisor confidence in the reliability and the representative nature of the sample charactieristics being reported.

Without exception, the final responsibility for the reliability of the analytical results submitted rests with the Laboratory Director.

1.3 Analytical Methods

In general, the widespread use of an analytical method indicates that it is a reliable means of analysis, and this fact tends to support the validity of the test result reported. Conversely, the use of a little-known technique forces the data user to place faith in the judgement of the analyst. When the analyst uses a "private" method, or one not commonly accepted in the field, he must stand alone in defining both his choice of the method and the result obtained.

The need for standardization of methods within a single laboratory is readily apparent. Uniform methods between cooperating laboratories are also important in order to remove the methodology as a variable in comparison or joint use of data between laboratories. Uniformity of methods is particularly important when laboratories are providing data to a common data bank, such as STORET*, or when several laboratories are cooperating in joint field surveys. A lack of standardization of methods raises doubts as to the validity of the results reported. If the same constituent is measured by different analytical procedures, within a single laboratory, or in several laboratories, the question is raised as to which procedure is superior, and why the superior method is not used throughout.

The physical and chemical methods used should be selected by the following criteria:

a. The method should measure the desired constituent with precision and accuracy sufficient to meet the data needs in the presence of the interferences normally encountered in polluted waters.

b. The procedure should utilize the equipment and skills normally available in the average water pollution control laboratory.

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*STORET is the acronym used to identify the computer-oriented U.S. Environmental Protection Agency Water Quality Control Information System for STOrage and RETrieval of data and information.

c. The selected methods should be in use in many laboratories or have been sufficiently tested to establish their validity.

d. The method should be sufficiently rapid to permit routine use for the examination of large numbers of samples.

The use of EPA methods in all EPA laboratories provides a common base for combined data between Agency programs. Uniformity throughout EPA lends considerable support to the validity of the results reported by the Agency.

Regardless of the analytical method used in the laboratory,the specific methodology should be carefully documented. In some water pollution reports it is customary to state that Standard Methods (1) have been used throughout. Close examination indicates, however, that this is not strictly true. In many laboratories, the standard method has been modified because of recent research or personal preferences of the laboratory staff. In other cases the standard method has been replaced with a better one. Statements concerning the methods used in arriving at laboratory data should be clearly and honestly stated. The methods used should be adequately referenced and the procedures applied exactly as directed.

Knowing the specific method which has been used, the reviewer can apply the associated precision and accuracy of the method when interpreting the laboratory results. If the analytical methodology is in doubt, the data user may honestly inquire as to the reliability of the result he is to interpret.

The advantages of strict adherence to accepted methods should not stifle investigations leading to improvements in analytical procedures. In spite of the value of accepted and documented methods, occasions do arise when a procedure must be modified to eliminate unusual interference, or to yield increased sensitivity. When modification is necessary, the revision should be carefully worked out to accomplish the desired result. It is advisable to assemble data using both the regular and the modified procedure to show the superiority of the latter. This useful information can be brought to the attention of the individuals and groups responsible for methods standardization. For maximum benefit, the modified procedure should be rewritten in the standard format so that the substituted procedure may be used throughout the laboratory for routine examination of samples. Responsibility for the use of a non-standard procedure rests with the analyst and his supervisor, since such use represents a departure from accepted practice.

In field operations, the problem of transport of samples to the laboratory, or the need to examine a large number of samples to arrive at gross values will sometimes require the use of rapid field methods yielding approximate answers. Such methods should be used with caution, and with a clear understanding that the results obtained do not compare in reliability with those obtained using standard laboratory methods. The fact that "quick and dirty" methods have been used should be noted, and the results should not be reported along with more reliable laboratory-derived analytical information. The data user is entitled to know that approximate values have been obtained for screening purposes only, and that the results do not represent the customary precision and accuracy obtained in the laboratory.

1.4 References

1. Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Association, New York (1971).

CHAPTER 2

LABORATORY SERVICES

2.1 General

Quality control of laboratory analyses involves consideration and control of the many variables which affect the production of reliable data. The quality of the laboratory services available to the analyst must be included among these variables. An abundant supply of distilled water, free from interferences and other undesirable contaminants, is an absolute necessity. An adequate source of clean, dry, compressed air is needed. Electrical power for routine laboratory use and voltage-regulated sources for delicate electronic instrumentation must be provided. This chapter, therefore, will be devoted to describing methods of maintaining the quality of these services, as used in laboratory operations.

2.2 Distilled Water

Distilled or demineralized water is used in the laboratory for dilution, preparation of reagent solutions, and final rinsing of glassware. Ordinary distilled water is usually not pure. It may be contaminated by dissolved gases and by materials leached from the container in which it has been stored. Volatile organics distilled over from the feed water may be present, and non-volatile impurities may occasionally be carried over by the steam, in the form of a spray. The concentration of these contaminants is usually quite small, and distilled water is used for many analyses without further purification. However, it is highly important that the still, storage tank, and any associated piping be carefully selected, installed, and maintained in such a way as to assure minimum contamination.

Water purity has been defined in many different ways, but one generally accepted definition states that high purity water is water that has been distilled and/or deionized so that it will have a specific resistance of 500,000 ohms (2.0 micromhos conductivity) or greater. This definition is satisfactory as a base to work from, but for more critical requirements, the breakdown shown in Table 2-1 has been suggested to express degrees of purity (1).

Table 2-1

WATER PURITY

Degree of Purity	Maximum Conductivity (micromhos/cm)	Approximate Concentration of Electrolyte (mg/1)
Pure	10	2-5
Very Pure	1	0.2-0.5
Ultrapure	0.1	0.01-0.02
Theoretically Pure	0.055	0.00

Properly designed metal stills from reputable manufacturers offer a convenient and reliable source of distilled water. These stills are usually constructed of copper, brass, and bronze. All surfaces that contact the distillate should be heavily coated with pure tin to prevent metallic contamination. The metal storage tank should be of sturdy construction, have a tight-fitting cover, and a filter in the air vent to remove airborne dust, gases, and fumes.

For special purposes, an all-glass distillation unit may be preferable to the metal still. These stills are usually smaller, and of more limited capacity than the metal stills. An actual comparison in which the distillates from an all-glass still and a metal still were analyzed spectrographically for certain trace metal contaminants is shown below in Table 2-2.

Table 2-2

COMPARISON OF DISTILLATES FROM GLASS AND METAL STILLS

	Element and Concentration (Micrograms/l)							
Source	Zn	B	Fe	Mn	Al	Cu	Ni	Pb
All-Glass Still	<1	12	1	<1	4	5	<1	<2
Metal Still	9	13	2	<1	<5	11	<2	26

It can be seen that the all-glass still produced a product which had substantially lower contamination from zinc, copper, and lead. Other analyses have indicated the same general relationship, except that a boron concentration of 100 micrograms/liter was found in water from the all-glass still on one occasion. This was probably related to the length of time the distillate had remained in the glass storage reservoir.

All stills require periodic cleaning to remove solids which have been deposited from the feed water. Hard water and high dissolved solids content promote scale formation in the evaporator, and cleaning frequency will thus depend on the quality of the feed water. The boiler of an all-glass still should be drained daily and refilled with clean water. Build-up of scale is easily detected, and the boiler and condenser coils should be cleaned at frequent intervals. Metal stills usually incorporate a constant bleeder device which retards scale formation to some extent. However, these units should still be dismantled and cleaned at regular intervals. Cleaning should always be in accordance with the manufacturer's instructions.

Pre-treatment of the incoming feed water will often improve still performance and raise the quality of the distillate. For example, preliminary softening of hard water removes calcium and magnesium prior to distillation. This reduces scale formation in the boiler and condenser, thereby reducing maintenance service. These softeners employ the ion exchange principle using a sodium chloride cycle, and are relatively inexpensive to operate. A carbon filtration system, installed at the feed water intake, will remove organic materials which might subsequently be carried over in the distillate. If trace concentrations of ions are a major concern, the distillate may be passed through a mixed-bed ion exchanger.

At least two commercially manufactured systems are available for production of high purity water by ion exchange. The Millipore Super-Q System (Millipore Corp., Bedford, Mass.), consists essentially of disposable cartridges for prefiltration, organic absorption, deionization and Millipore filtration. The company claims it can produce 10 megohm water, containing no particulate matter larger than 0.45 micron in size, from tap water, at the rate of 20 gallons per hour. Continental Water Conditioning Corp., El Paso, Texas, advertises a system which can be tailored to the needs of the customer. Performance specifications include minimum flow rates of 45 gallons per hour and total dissolved solids of less than 0.1 mg/1 when required.

Specific conductance is a rapid and simple measurement for determining the inorganic quality of distilled water. Stills of the types previously discussed are capable of producing a distillate with a specific conductance of less than 2.0 micromhos at 25° C. This is equivalent to 0.5-1.0 mg/1 of ionized material. Frequent checks should be made to determine that optimum performance is being maintained. A purity meter installed between the still and the storage reservoir will monitor the conductivity of the distillate, in terms of the equivalent in mg/1 of sodium chloride. If the reading on the meter begins to rise above the present limit of conductivity, effective action should be taken to eliminate the source of contamination. Organic quality is more difficult to monitor, but the total organic carbon determination is a simple and rapid test for organic contaminants.

A piping system for delivering distilled water to the area of use within the laboratory is a convenient and desirable feature. In this case, special care should be taken that the quality of the water is not degraded between the still and the point of use. Piping may be of tin, tin-lined brass, stainless steel, plastic, or chemically resistant glass, depending on the quality of the water desired and on available funds. Tin is best, but is also very expensive. As a compromise, plastic pipe, or glass pipe with Teflon* O-rings at all connecting joints is satisfactory for most purposes. The glass pipe has an obvious advantage when freedom from trace amounts of organic materials is important.

When there is no piped-in supply, distilled water will probably be transported to the laboratory and stored in polyethylene or glass bottles of about 5-gallon capacity. If stored in glass containers, distilled water will gradually leach the more soluble materials from the glass and cause an increase in dissolved solids. Therefore, only borosilicate-free glass containers should be used. Polyethylene bottles contain organic plasticizers, and traces of these materials may be leached from the container walls. These are of little consequence, except in some organic analyses. Rubber stoppers often used in storage containers contain leachable materials, including significant quantities of zinc. This is usually no problem, since the water is not in direct contact with the stopper. However, the analyst should be aware of the potential for contamination, especially when the supply is not replenished by frequent use.

The delivery tube may consist of a piece of glass tubing which extends almost to the bottom of the bottle, and which is bent downward above the bottle neck, with a three-to-four-foot piece of flexible tubing attached for mobility. Vinyl tubing is preferable to latex rubber, because it is less leachable. However, a short piece of latex tubing may be required at the outlet for better control of the pinchcock. The vent tube in the stopper should be protected against the entrance of dust.

Ordinary distilled water is quite adequate for many analyses, including the determination of major cations and anions. Certain needs may require the use of double- or even triple-distilled water. Redistillation from an alkaline permanganate solution can be used to obtain a water with low organic background. When determining trace organics by solvent extraction and gas chromatography, distilled water with sufficiently low background may be extremely difficult to obtain. In this case, pre-extraction of the water with the solvent used in the respective analysis may be helpful in eliminating undesirable peaks in the blank.

**Trademark of E.I. duPont de Nemours & Co.*

Certain analyses require special treatment or conditioning of the distilled water, and these will now be discussed.

2.3 Ammonia-Free Water

Removal of ammonia can be accomplished by shaking ordinary distilled water with a strong cation exchanger, or by passing distilled water through a column of such material. For limited volumes of ammonia-free water, use of the Quikpure (Box 254, Chicago, Ill.) 500-ml bottle is highly recommended. The ion-free water described below is also suitable for use in the determination of ammonia.

2.4 Carbon-Dioxide-Free Water

Carbon-dioxide-free water may be prepared by boiling distilled water for 15 minutes and cooling to room temperature. As an alternative, distilled water may be vigorously aerated with a stream of inert gas for a period sufficient to achieve saturation and CO_2 removal. Nitrogen is most frequently used. The final pH of the water should lie between 6.2 and 7.2. It is not advisable to store CO_2-free water for extended periods.

2.5 Ion-Free Water

A multi-purpose high purity water, free from trace amounts of the common ions, may be conveniently prepared by slowly passing distilled water through an ion-exchange column containing one part of a strongly acidic cation-exchange resin in the hydroxyl form. Resins of a quality suitable for analytical work must be used. Ion-exchange cartridges of the research grade, available from scientific supply houses, have been found satisfactory. By using a fresh column and high quality distilled water, a water corresponding to the ASTM designation for referee reagent water (2) (maximum 0.1 mg/1 total matter and maximum conductivity of 0.1 micromho) can be obtained. This water is suitable for use in the determination of ammonia, trace metals, and low concentrations of most cations and anions. It is not suited to some organic analyses, however, because this treatment adds organic contaminants to the water by contact with the ion-exchange materials.

2.6 Compressed Air

The quality of compressed air required in the laboratory is usually very high, and special attention should be given to producing and maintaining clean air until it reaches the outlet. Oil, water, and dirt are undesirable contaminants in compressed air, and it is important to install equipment which generates dry, oil-free air. When pressures of less than 50 psi are required, a rotary-type compressor, using a water seal and no oil, eliminates any addition of oil which would subsequently have to be removed from the system. Large, horizontal, water-cooled compressors will usually be used when higher pressures are required.

Compression heats air, thus increasing its tendency to retain moisture. An aftercooler is therefore necessary to remove water. Absorption filters should be used at the compressor to prevent moisture from entering the piping system. Galvanized steel pipe with threaded, malleable-iron fittings, or solder-joint copper tubing should be used for piping the air to the laboratory.

When the compressed air entering the laboratory is of low quality, an efficient filter should be installed between the outlet and the point of use to trap oil, moisture, and other contaminants. As an alternative, high quality compressed air of the dry grade is commercially available in cylinders when no other source exists.

2.7 Electrical Services

An adequate electrical system is indispensable to the modern laboratory. This involves having both 115- and 230-volt sources in sufficient capacity for the type of work that must be done. Requirements for satisfactory lighting, proper functioning of sensitive instruments, and operation of high current devices must be considered. Any specialized equipment may present unusual demands on the electrical supply.

Due to the special type of work, requirements for a laboratory lighting system are quite different from those in other areas. Accurate readings of glassware graduations, balance verniers, and other measuring lines must be made. Titration endpoints, sometimes involving subtle changes in color or shading, must be observed. Levels of illumination, brightness, glare, and location of light sources should be controlled to facilitate ease in making these measurements and to provide maximum comfort for the employees.

Spectrophotometers, flame photometers, atomic absorption equipment, emission spectrographs, gas chromatographs, etc. have complicated electronic circuits which require relatively constant voltage to maintain stable, drift-free instrument operation. If the voltage to these circuits varies, there is a resulting change in resistance, temperature, current, efficiency, light output, and component life. These characteristics are interrelated, and one cannot be changed without affecting the others. Voltage regulation is therefore necessary to eliminate these conditions.

Many instruments have built-in voltage regulators which perform this function satisfactorily. In the absence of these, a small, portable, constant-voltage transformer should be placed in the circuit between the electrical outlet and the instrument. Such units are available from Sola Basic Industries, Elk Grove Village, Ill., and are capable of supplying a constant output of 118 volts from an input which varies between 95 and 130 volts. When requirements are more stringent, special transformer-regulated circuits can be used to supply constant voltage. Only the instrument receiving the regulated voltage should be operated from such a circuit at any given time. These lines are in addition to, and separate from the ordinary circuits used for operation of equipment with less critical requirements.

Electrical heating devices provide desirable heat sources, and should offer continuously variable temperature control. Hot plates and muffle furnaces wired for 230-volt current will probably give better service than those which operate on 115 volts, especially if the lower voltage circuit is only marginally adequate. Water baths and laboratory ovens with maximum operating temperatures of about 200°C perform well at 115 volts. Care must be taken to ground all equipment which could constitute a shock hazard. The three-pronged plugs which incorporate the ground are best for this purpose.

2.8 References

1. Applebaum, S. B., and Crits, G. J., "Producing High Purity Water." Industrial Water Engineering, Sept./Oct. 1964.

2. 1968 Book of ASTM Standards, Part 23, Atmospheric Analysis, pp. 225-6, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103.

CHAPTER 3

INSTRUMENTAL QUALITY CONTROL

3.1 Introduction

The modern analytical laboratory depends very heavily upon instrumentation. This statement may be completely obvious, but it should be remembered that the exceptional emphasis on electronic equipment has really begun since the development of the transistor and the computer. Analytical instrumentation, to a certain extent, is always in the development stage, with manufacturers continually redesigning and upgrading their products, striving for miniaturization, better durability and sensitivity, and improved automation. The net result to laboratory supervisors and staff members is a bewildering stream of advertising brochures, announcements, and catalogues of newly available equipment. Consequently, the selection and purchase of analytical equipment is, at all times, beset with uncertainty.

Table 3-1 lists the instruments most commonly used for water and wastewater analysis. These represent basic equipment used in routine work and should be the subject of careful consideration before purchase. Further, operation and maintenance of these devices ought to be a primary consideration in production of satisfactory data. Obviously, a fundamental understanding of instrument design will assist the analyst in the correct use of the instrument and in some cases aid in detecting instrumental failures.

In the pages that follow an attempt is made to discuss basic instrument design and to offer some remarks whenever possible about desirable instrumental features.

Table 3-1

INSTRUMENTS COMMONLY USED
IN WATER AND WASTEWATER ANALYSIS

- Analytical Balance
- Potentiometer (pH meter)
- Conductivity meter
- Turbidimeter
- Spectrophotometers
  - a. Visual
  - b. Ultraviolet
  - c. Infrared
  - d. Atomic absorption
- Total Carbon Analyzer
- Gas Chromatographs
- Miscellaneous
  - a. Temperature devices (ovens, water baths, etc.)
  - b. Recorders
  - c. Selective Ion Electrodes

3.2 Analytical Balances

The most important piece of equipment in any analytical laboratory is the analytical balance (See Figure 3-1). It bears the same relationship to accuracy of measurements produced by a laboratory as the Greenwich standard clock has to international time-keeping. If the balance is not accurate all data related to weight-prepared standards will contain the same degree of error. The balance, therefore, should be the most protected and cared-for instrument in the laboratory. Unfortunately, care of the balance is frequently overlooked.

There are many fine balances on the market designed to meet a variety of needs such as sensitivity, speed weighing, batch weighing, etc. Types of balances include general purpose, micro-, electro-, semi-analytical, analytical and other special purpose instruments. Each type of balance has its own place in the scheme of laboratory operation but the analytical balance is by far the most important in the production of reliable data.

Most analytical balances in use today in well equipped laboratories are of the "single pan" variety. Single-pan capacities range from 80 grams to the popular 200-gram models with sensitivities from 0.01 to 1 mg. Features of single-pan balances include mechanical lifting and substitution of weights, digital readout of weights, and mechanical zeroing of the empty balance. The advantage of the single-pan balance over the old "two-pan" balance is in greatly increased weighing speed and improved weighing accuracy because of mechanical weight handling. With all the design improvements, however, the modern analytical balance is still a fragile instrument, subject to shock, temperature and humidity changes, mishandling and various other insults. Some of the precautions to be observed in maintaining and prolonging the dependable life of a balance are as follows:

a. Analytical balances should be mounted on a heavy shock-proof table, preferably one with adequate working surface and a suitable drawer for storage of balance accessories; balance level should be checked frequently and adjusted when necessary.

b. Balances should be located away from laboratory traffic, protected from sudden drafts and humidity changes.

c. Balance temperatures should be equilibrated with room temperature; this is especially important if building heat is shut off or reduced during non-working hours.

d. When not in use, the beam should be raised from the knife edges, the weights returned to the beam, objects such as weighing dish removed from the pan, and the slide door closed.

e. Special precautions should be taken to avoid spillage of corrosive chemicals on the pan or inside the balance case; the interior of balance housing should be kept scrupulously clean.

f. Balances should be checked and adjusted periodically by a company service man or balance consultant; if service is not available locally, follow the manufacturer's instructions as closely as possible.

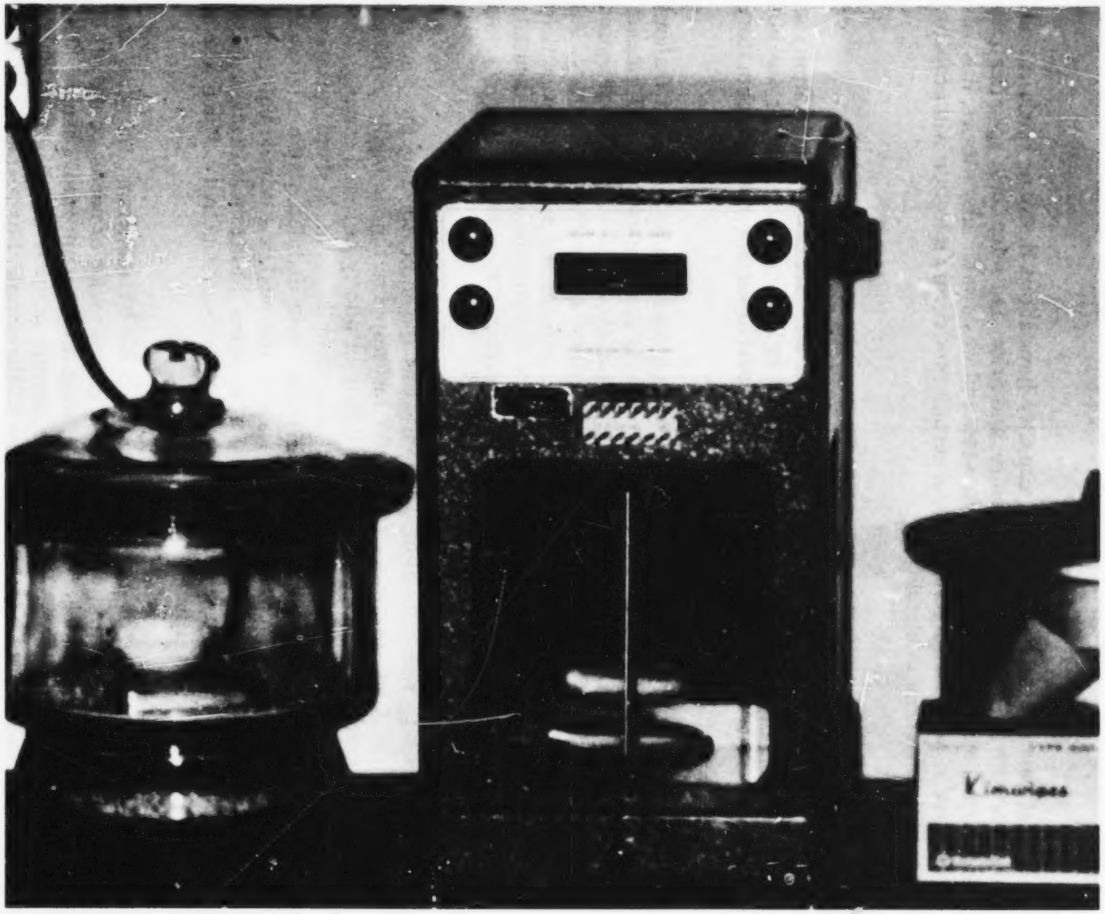

Figure 3-1. ANALYTICAL BALANCE

g. The balance should be operated at all times according to the manufacturer's instructions.

Standardized weights to be used in checking balance accuracy, and that meet U.S. Bureau of Standards specifications, may be purchased from various supply houses. A very complete set of directions for checking the performance of a balance is contained in Part 30 of ASTM Standards (1).

Since all analytical balances of the 200-gram capacity have about the same specifications with reference to sensitivity, precision, convenience, and price, and since these specifications are suitable for normal weighing requirements in water and wastewater laboratories, it is safe to assume that there is no clear preference for a certain model, and selection will probably be made on the basis of service availability.

3.3 pH Meters

The concept of pH as a means of expressing the degree of effective acidity or alkalinity as contrasted with total acidity or alkalinity was developed by Sorenson in 1909. It was not until about 1940 that commercial instruments were developed for routine laboratory measurement of pH.

A basic pH meter (See Figure 3-2) consists of a voltage source, amplifier, and readout device, either scale or digital. Certain additional refinements produce varying performance characteristics between models. Some models incorporate expanded scales for increased readability and solid state circuitry for operating stability and extreme accuracy. All instruments of recent design also include temperature adjustment and slope adjustment to correct for asymmetric potential of glass electrodes. Other features are scales that facilitate use of selective ion electrodes, recorder output, and interfacing with complex data handling systems.

In routine analytical work, the glass electrode is used as the indicator and the calomel electrode as the reference. Glass electrodes have a very fast response time in highly buffered solutions. However, accurate readings are obtained slowly in poorly buffered samples, and particularly when changing from buffered to unbuffered samples, as after standardization. Electrodes, both glass and calomel, should be well rinsed with distilled water after each reading, and should be rinsed or dipped several times into the next test sample before the final reading is taken. Weakly buffered samples should be stirred during measurement. Glass electrodes should not be allowed to become dry during periods of inactivity. When not in use they should be immersed in distilled water.

The first step in standardization of the instrument is done by immersing the glass and calomel electrodes into a buffer of known pH, setting the meter scale or needle to the pH of the buffer and adjusting the proper controls to bring the circuit into balance. The temperature compensating dial should be set at the sample temperature. The pH of the standard buffer should be within about two pH units of the sample. For best accuracy, the instrument should be calibrated against two buffers that bracket the pH of the samples.

The presence of a faulty electrode is indicated by failure to obtain a reasonably correct value for the pH of the second reference buffer solution after the meter has been standardized with the first. A cracked glass electrode will often yield pH readings that are essentially the same for both standards. The response of electrodes may also be impaired by

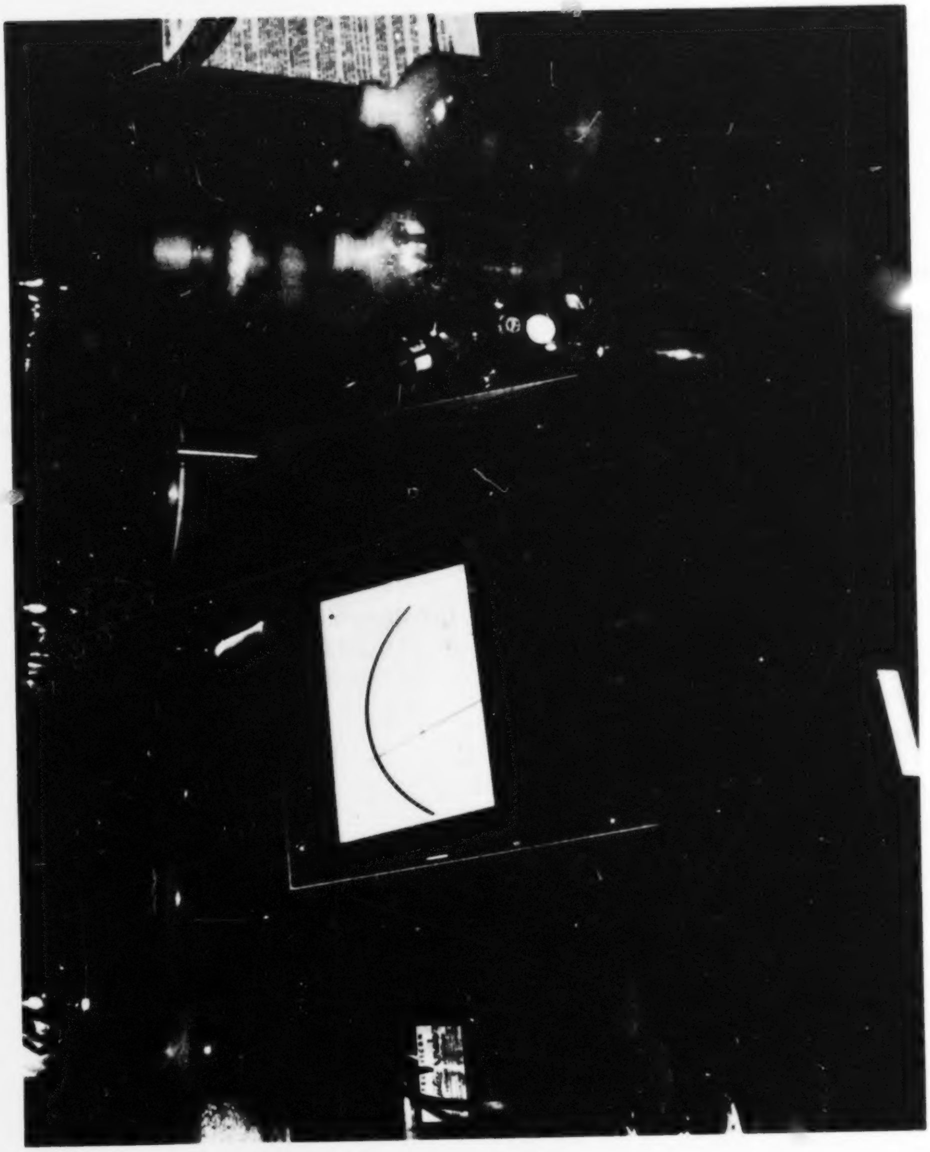

Figure 3-2. pH METER

failure to maintain the KCl level in the calomel electrode, or by certain specific materials such as oily substances and precipitates that may coat the surfaces. A faulty condition can be recognized from the check with the two buffer solutions. If either of these conditions should occur the electrode can probably be restored to normal by an appropriate cleaning procedure. Complete and detailed cleaning methods are given in Part 23 of ASTM Standards (2).

Because of the asymmetric potential of the glass electrode most pH meters are built with a "slope adjustment" which enables the analyst to correct for slight electrode errors that occur when standardization is performed at two different pH levels. Exact details of slope adjustment and slope check may vary with different models of instruments. The slope adjustment must be made whenever electrodes are changed, subjected to vigorous cleaning, or refilled with fresh electrolyte. The slope adjustment feature is highly desirable and recommended for consideration when purchasing a new meter.

Most pH meters now available are built with transistorized circuits rather than vacuum tubes which greatly reduces warm-up time and increases stability of the meter. Also, many instruments are designed with a switching circuit so that the conventional 0-14 scale may be used to read a single pH unit. The "expanded-scale" feature allows for more accurate readings and may be of definite value when the meter is used for potentiometric titrations. It is of dubious value, however, in routine analytical work, since readings more percise than ± 0.1 pH are seldom required.

Solid state circuitry has led to improved design of compact instruments suitable for field work. Field-type instruments are generally battery-powered, and require more maintenance and more frequent standardization than laboratory instruments.

Standard buffer solutions, covering a range of pH, may be purchased from almost any chemical supply house and are completely satisfactory for routine use. Table 3-2 below gives a list of NBS buffers (easily made in the laboratory) and the resulting pH at several different temperatures.

Table 3-2

pH VALUES OF NBS STANDARDS FROM 0 - 30°C

Temp. °C	0.05M Potassium Tetroxalate	Potassium Acid Tartrate (Sat. at 25°C)	0.05 M Potassium Acid Phthalate	0.025 M Potassium Dihydrogen Phosphate + 0.025 M Sodium Dihydrogen Phosphate	0.01 M Sodium Tetraborate
0	1.67	–	4.01	6.98	9.46
10	1.67	–	4.00	6.92	9.33
15	1.67	–	4.00	6.90	9.27
20	1.68	–	4.00	6.88	9.22
25	1.68	3.56	4.01	6.86	9.18
30	1.69	3.55	4.01	6.85	9.14

Some idea of the effect of temperature on pH may be obtained by observing temperature vs pH of various buffers shown in the table. Theoretically, the potential response of the electrode system changes 0.20 mV per pH unit per degree centigrade. Since all pH meters measure potential but read out in pH, a variable compensation is used. A rough rule of thumb is that temperature compensation is about 0.05 pH units per 5 degree increase in temperature.

Typical performance data of a conventional expanded scale pH meter is shown in Table 3-3 below.

Table 3-3

PERFORMANCE CHARACTERISTICS OF TYPICAL pH METER

	Normal Scale	Expanded Scale
Range	0 to 14 pH ±1400 mv	1 pH ±100 mv
Smallest scale division	0.1 pH 10 mv	0.005 pH 0.5 mv
Accuracy	±0.05 pH ±5 mv	±0.002 pH ±2% of reading
Reproducibility	±0.02 pH ±2 mv	±0.002 pH ±0.2 mv
Temp. compensation	0 to 100°C (manual or automatic)	
Input impedance	$>10^{14}$	$>10^{13}$
Power requirements	115/220V, 50/60 Hz	
Dimensions	12½" w x 11" d x 8¼" h	

3.4 Conductivity Meters

Solutions of electrolytes conduct an electric current by the migration of ions under the influence of an electric field. For a constant applied EMF, the current flowing between opposing electrodes immersed in the electrolyte will vary inversely with the resistance of the solution. The reciprocal of the resistance is called conductance and is expressed in reciprocal ohms or mhos. For natural water samples where the resistance is high, the usual reporting unit is in micromhos. Figure 3-3 shows a typical conductivity meter.

The passage of direct current through an electrolyte causes changes in the electrolyte, hence, to prevent polarization, it is necessary to use an alternating current or current pulses of short duration when measuring conductivity. Originally, conductivity meters were built using a rapidly alternating current of low intensity in the audio range, and were equipped

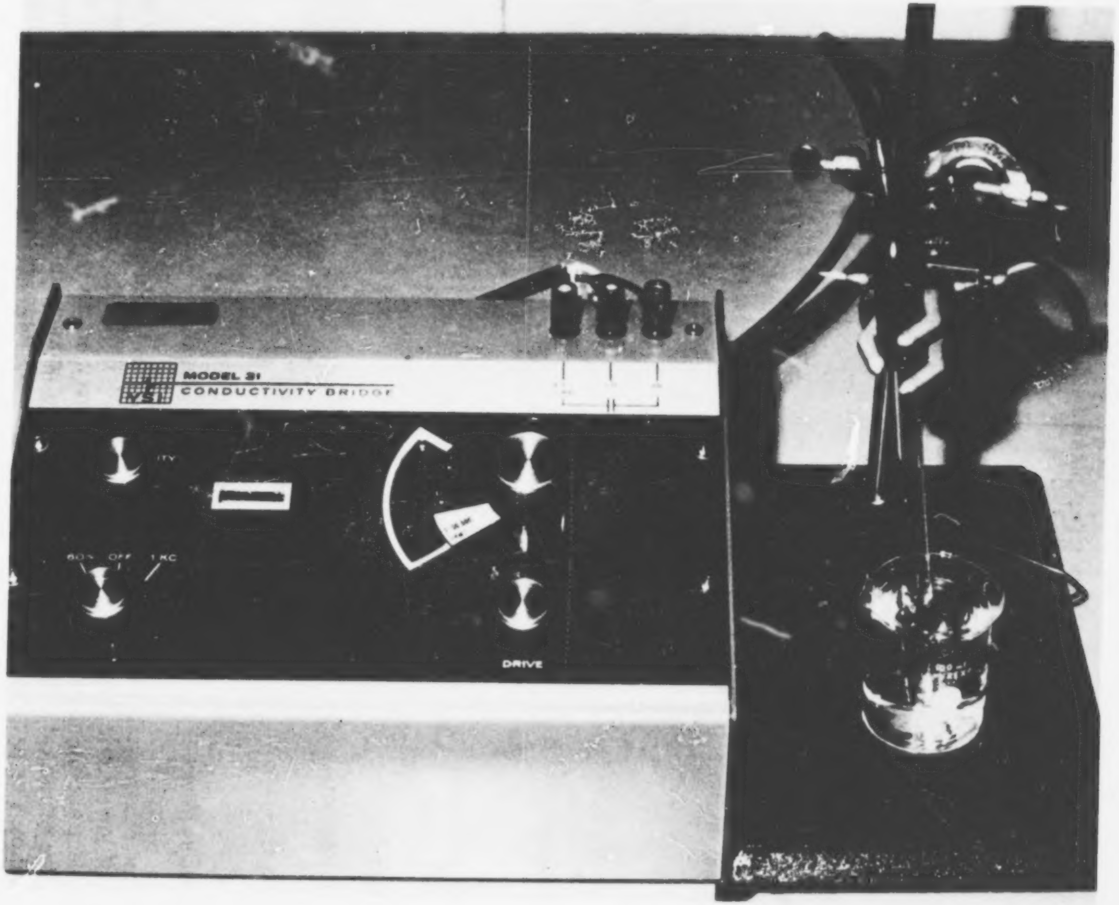
YSI
MODEL 31
CONDUCTIVITY BRIDGE
60~ OFF 1KC
DRIVE

Figure 3-3. CONDUCTIVITY METER

with balance. For obvious reasons, the earpiece has been replaced by other devices, such as the cathode ray tube commonly known as the "magic eye". Practically all conductivity meters on the present market use some variation of the "magic eye" for indicating solution conductivity, and include a stepping switch for varying resistances in steps of 10X. The instruments are therefore capable of reading conductivities from about 0.1 μ mhos to about 250,000 μ mhos.

The sensing element for a conductivity measurement is the conductivity cell, which normally consists of two thin plates of platinized metal, rigidly supported with a very precise parallel spacing. For protection, the plates are mounted inside a glass tube, with openings in the side walls and submersible end for access of sample. Variations in designs have included use of hard rubber and plastics for protection of the cell plates. Glass may be preferable, in that the plates may be visually observed for cleanliness and possible damage, but the more durable encasements have the advantage of greater protection and reduced cell breakage. One manufacturer offers a cell containing circular carbon plates embedded in an epoxy-type plastic. Reversing the usual procedures, the sample is poured into the cell. The cell is particularly attractive because of its ruggedness and the fact that it can be cleaned without changing the cell factor.

Special precaution is taken with the arrangement of lead wires from the plates. Since stray electrolytic and capacitive current will pass between them, thereby distorting the bridge balance, the wires must be properly separated, usually by use of a non-conducting bead or collar on one of the lead wires.

In routine use, cells should be frequently examined to insure that (a) platinized coating of plates is intact, (b) plates are not coated with suspended matter, (c) plates are not bent, distorted, or misaligned, and (d) lead wires are properly spaced.

Temperature has a pronounced effect on the conductance of solutions, and must be corrected when results are reported. The specified temperature for reporting data used by most analytical groups (and all EPA laboratories) is 25°C. Data correction may be accomplished by adjusting sample temperatures to 25°C., or by use of mathematical or electronic adjustment. Adjustment of sample temperature is the preferred system, because of the empirical nature of the mathematical correction. However, investigative work in the Analytical Quality Control Laboratory, and at the upper Ohio Basin Office, EPA, has shown that acceptable data is obtained if conductivity readings taken at stream-side are electronically temperature-corrected to 25°C.

Instrumental troubles are seldom encountered with conductivity meters because of the design simplicity. When troubles occur they are usually in the cell, and for most accurate work the following procedures should be used:

a. Standardize the cell and establish a cell factor by measuring the conductivity of a standard potassium chloride solution (standard conductivity tables may be found in various handbooks).

b. Rinse the cell by repeated immersion in distilled water.

c. Again, immerse the cell in the sample several times before obtaining a reading.

d. If the meter is equipped with a "magic eye", determine the maximum width of the shadow at least twice, by approaching the endpoint from a low reading upward, and from a high reading downward.

Because the cell constants are subject to slow change, even under ideal conditions, and sometimes to more rapid change under adverse conditions, it is recommended that the cell constant be periodically established. Table 3-4, below, can be used for this operation.

Table 3-4
ELECTRICAL CONDUCTIVITY OF POTASSIUM CHLORIDE REFERENCE SOLUTIONS

Solution	Normality	Method of Preparation	Temp. (°C)	Conductivity (μ mhos)
A	0.1	7.4365 g KCl/l at 20°C	0	7,138
			18	11,167
			25	12,856
B	0.01	0.7440 g KCl/l at 20°C	0	773
			18	1,220
			25	1,408
C	0.001	Dilute 100 ml of B to 1 l at 20°C	25	147

For instruments reading in mhos, calculate the cell constant as follows:

$$L = \frac{K_1 + K_2}{1{,}000{,}000 \times K_X}$$

where

L = cell constant

K_1 = Conductivity, in μ mhos/cm, of the KCl solution at the temperature of measurement

K_2 = conductivity, in μ mhos, at the same temperature, of the distilled water used to prepare the reference solution

K_X = measured conductance, in mhos

Conductivity equipment which has generally been found to be reliable for laboratory work includes the YSI #31 (Yellow Springs Instrument Co., Box 279, Yellow Springs, Ohio 45387), the Lab-Line Mark IV #1100 and MC3 #11025 (Lab-Line Instruments Inc., 15th & Bloomingdale Aves., Melrose Park, Ill. 60160), and Industrial Instruments #RC 16B2 and RC-18 (Industrial Instruments Inc., 89 Commerce Road, Cedar Grove, N.J. 07009).

The YSI #31 is particularly suitable for routine lab work because of the brilliance of the magic eye. The Lab-Line meters provide the sturdy cell previously mentioned. The Industrial Instruments #RC-18 is designed for extreme accuracy but the number of dial settings required to obtain a single reading do not recommend it for routine analysis. A recent instrument survey conducted by the Methods and Performance Activity of the Analytical Quality Control Laboratory showed that a preponderance of EPA Laboratories used the Industrial Instruments RC 16B2.

3.5 Turbidimeters

Instruments for the measurement of turbidity have traditionally employed principles of design related to transmission or reflectance of light. The lack of a primary standard for turbidity, however, has resulted in a complete absence of uniformity among the available instruments. Further, the Jackson Candle Turbidimeter, which does not depend upon the use of a primary standard, is a primitive instrument, subject to many interferences, and the measurements generally are not reproducible.

Recent investigations (3) have resulted in the design of an instrument which has been adopted by the Environmental Protection Agency as a standard. The specifications for the instrument are described elsewhere (4). Presently, the Hach Turbidimeter, Model 2100, (Box 907, Ames, Iowa 50010) is the only turbidity measuring device manufactured which meets these specifications. Figure 3-4 shows this instrument.

The Hach Turbidimeter Model 2100 employs, for standardization, a suspension of formazin, especially used because of its stability and uniform particle size. For calibration purposes, the formazin is permanently embedded in a cylinder of lucite, the cylinder duplicating the size and shape of the sample cuvette. Although the instrument is designed with a series of scales ranging 0-1, 0-10, 0-100 and 0-1000 JCU, it has been recommended that turbidity readings in excess of 40 JCU be rejected (3). Correct use of the meter therefore requires that samples containing turbidities in excess of 40 JCU be diluted to a value below this level and the results multiplied by the proper dilution factor.

For production of data with maximum accuracy and precision the following precautions should be observed:

a. Protect the lucite standard from nicks, scratches and fingerprints.

b. Use a constant orientation of the lucite standard while calibrating the instrument.

c. Use a well mixed sample in the sample cuvette; do not take readings until finely dispersed bubbles have disappeared.

d. Dilute samples containing excess turbidity to some value below 40 JCU; take reading, and multiply results by correct dilution factor.

3.6 Spectrophotometers

Since a large portion of routine quantitative measurements are performed colorimetrically, the spectrophotometer (See Figure 3-5) is usually the workhorse of any analytical laboratory. Indeed, the versatility of the instrument, and the number of demands imposed upon it, have resulted in a large variety of designs and price ranges. A systematic listing and detailed discussion of all instrumental types would be beyond the scope of this chapter. As a matter of convenience and practicality, therefore, spectrophotometers are discussed separately as visible, ultraviolet, infrared, and atomic absorption instruments.

A spectrophotometer is an instrument for measuring an amount of light or radiant energy transmitted through a solution, as a function of wave-length. A spectrophotometer differs

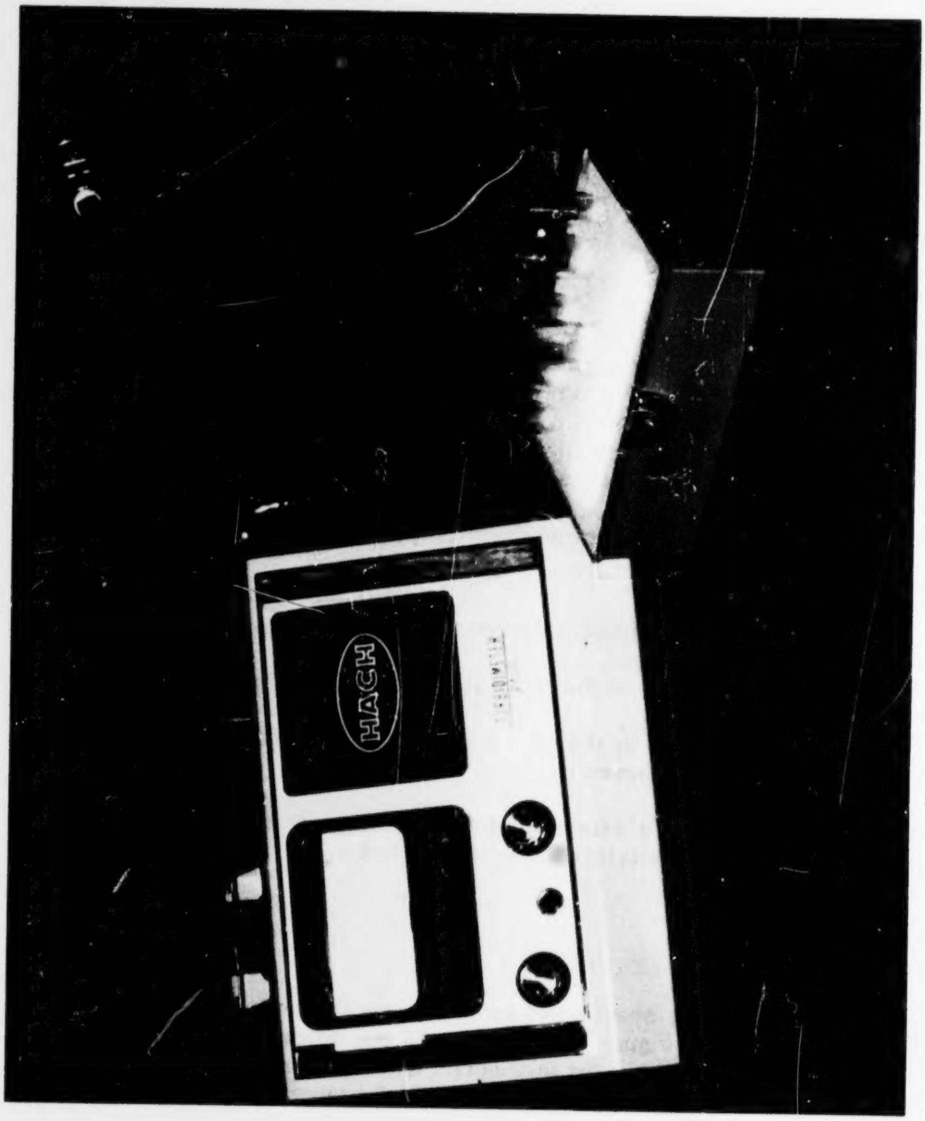

Figure 3-4. TURBIDIMETER

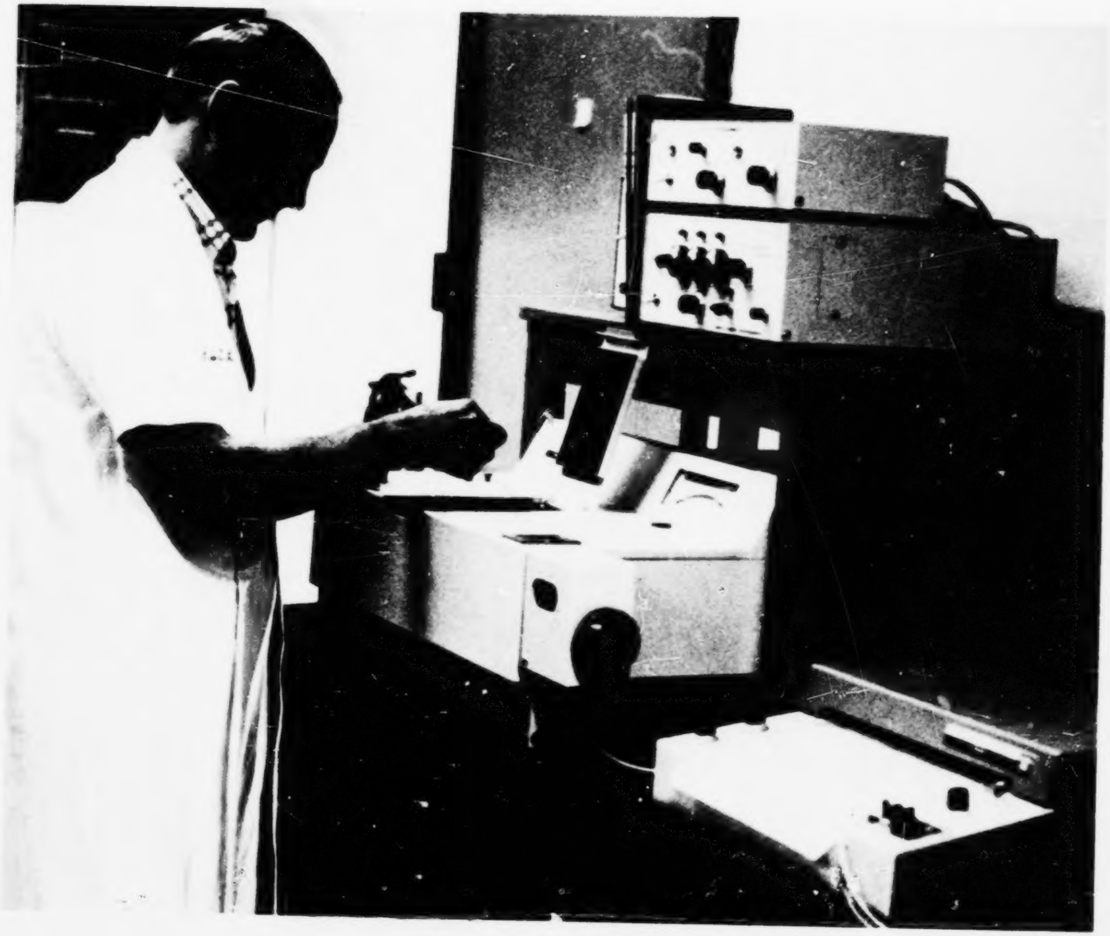

Figure 3-5. SPECTROPHOTOMETER

from a filter photometer in that it uses continuously variable, and more nearly monochromatic, bands of light. Filter photometers are relatively insensitive, and lack the versatility of spectrophotometers. They are used most profitably where a single method can be designed to fit the instrument.

The essential parts of a spectrophotometer are:

a. A source of radiant energy, usually a tungsten filament bulb,

b. The Monochromator, a device for isolating narrow bands of light,

c. Cells (cuvettes), for holding the colored solution under investigation, and

d. The photodetector, a device to detect and measure the radiant energy passing through the sample solution.

Each of the essential features listed, especially the monochromator and the photodetector system, vary in design principles from one instrument to another. Table 3-5 shows some of the features of the more commonly used spectrophotometers.

3.6.1. Visible Range

Desirable features on a visible-range spectrophotometer are determined by the anticipated use of the instrument. Simple, limited programs requiring use of only a few parameters at gross concentrations, can probably be supported by an inexpensive, but reliable instrument, such as the B&L Spectronic 20. (See Table 3-5.) On the other hand, if a laboratory program requires a wide variety of measurements on diverse samples at very low concentrations, a more versatile instrument may be needed. One of the prime considerations would be adaptability to various cell sizes, at least from 1.0 to 5.0 cm. Many spectrophotometers now available are satisfactory for water quality analyses.

As shown in Table 3-5, which lists only a few of the available spectrophotometers, higher priced instruments strive for versatility, including interchangeable sources, detectors, and cells. Complete information on instrument specifications can be found in the publication Industrial Research (Beverly Shores, Ind. 46301), Nov. 20, 1969.

3.6.2. Ultraviolet Range

An ultraviolet spectrophotometer is similar in design to a visual range instrument, differences being in the light source and the optics. The light source is a hydrogen or deuterium discharge lamp which emits radiations in the UV portion of the spectrum, generally from about 200 mμ to the low visible region. The optical system, if of the prism type, must be constructed of UV-transparant material, usually quartz. Sample cells must also be constructed of quartz or other UV-transparent material. If a grating system is used in an UV system, the grating may be specially cut (blazed) in the UV region for greater sensitivity. A number of UV spectrophotometers are available: the Beckman DU, the Hitachi, the Bausch and Lomb, the Cary, the Hilger and the Leeds & Northrup.

3.6.3. Infrared Range

A number of instrumental changes are required in the construction of spectrophotometers

Table 3-5

DESIGN FEATURES OF SOME COMMON SPECTROPHOTOMETERS

	Beckman B	Beckman Du	Bausch & Lomb Spectronic 20	Coleman 101	Hitachi [1]
Light Source	Tungsten Bulb from CV Transformer	Tungsten Bulb, CV Transformer Hydrogen Lamp	Tungsten Bulb, Reg. Transformer	Tungsten Bulb, CV Transformer Hydrogen (Deuterium) Lamp	Tungsten Bulb Hydrogen (Deuterium) Lamp
Optical System	Glass Prism	Quartz Prism	Grating, 600/mm	Grating, 600/mm	Grating, 1440/mm, Blazed at 200 mμ
Slits	Variable	Variable	Fixed, band width 20 mμ	Fixed, band width 10 mμ	Variable
Range	320-1000 mμ	200-1000 mμ	325-1000 mμ	220-900 mμ, using both lamps	195-950 mμ, using both lamps
Detector	Interchangeable Phototubes 320-625 and 625-1000 mμ	Interchangeable Phototubes 200-625 and 625-1000mμ	Interchangeable Phototubes 325-625 and 625-1000 mμ	Hitachi Dual Range Phototube, 220-900 mμ	Dual Range Phototube 195-950 mμ
Sample Cells	1.0 to 5.0 cm	1.0, 5.0, 10.0 cm	1.1, 1.6, 2.2 cm	1.0, 5.0, 20.0 cm	1.0 to 10.0 cm, micro cells
Readout	Meter Scale, %T, O.D.	Null Point Potentiometer, %T, O.D.	Meter Scale %T, O.D.	Meter Scale, %T, O.D.	Meter Scale, %T, O.D.
Attachment	Test-tube adapter flame photometry	UV Adapter with H_2 lamp flame photometry	Interchangeable test-tube adapters, digital readout, reflectance adapter	Recorder jack or digital readout	Atomic absorption reflectance, fluorescence, emission, flow thru cells

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(1) Marketed as Perkin-Elmer #139 or Coleman #139-001

for measurements in the infrared (IR) region. Modifications are needed, because optical materials, such as glass and quartz, absorb radiant energy in the IR region and ordinary photocells do not respond.

Most IR spectrophotometers use front-surfaced mirrors to eliminate the necessity for radiant energy to pass through quartz, glass, or other lens materials. The mirrors are usually parabolic to facilitate gathering the diffuse IR energy. Instruments must be protected from high humidities and water vapor to avoid deterioration of the optical system, and also to avoid extraneous absorption bands in the IR.

The energy or light source for an IR instrument may be a Nernst glower or a Globar. Either source has certain characteristics that recommend it for use, but the Globar is more commonly used because it has a more stable emission and it is more rugged. Receiving or detection units may be a thermocouple, a bolometer, thermistor, or a photoconductor cell.

Of all the IR instruments available, two are in relatively common use in EPA laboratories. The Perkin-Elmer Infracord is a low cost model designed for routine work with simplicity of operation. The Perkin Elmer #621 (723-G Main Ave., Norwalk, Conn., 06852) is a far more sophisticated instrument, designed for basic research.

3.6.4 Proper Use of Spectrophotometers

The manufacturer's instructions for proper use should be followed in all cases. Several safeguards against misuse of the instruments, however, are mandatory.

Instruments should be checked for wavelength alignment. If a particular colored solution is to be used at a closely specified wavelength, considerable loss of sensitivity can be encountered if the wavelength control is misaligned. In visual instruments, an excellent reference point is the maximum absorption for a dilute solution of potassium permanganate, which has a dual peak at 526 mμ and 546mμ. On inexpensive grating instruments, which possess less resolution than the prism instruments, the permanganate peak appears at 525 to 550 mμ as a single flat-topped spike.

For both UV and IR instruments, standard absorption curves for many organic materials have been published so that reference material for standard peaks is easily available. Standard films of styrene and other transparent plastics are available for IR wavelength checks.

Although most instruments contain built-in transformers for stabilization of the electronic circuits, an exterior, high capacity, constant-voltage transformer is recommended for general laboratory control. A number of controlled-voltage outlets in the laboratory are especially desirable in industrial areas or in buildings containing heavy, electrically operated equipment where voltage surges on adjacent power lines are apt to be frequent. An unstable voltage is frequently indicated by a flickering needle on the meter. The flickering behavior may be intermittent or it may occur at certain times of the day when heavy machinery in the area may be starting or stopping.

Too much emphasis cannot be placed on care of absorption cells. All cells should be kept scrupulously clean, free of scratches, fingerprints, smudges and evaporated film residues. Matched cells should be checked to see that they are equivalent by placing portions of the

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same solution in both cells and taking several readings of the %T or OD values. If a cell is mismatched it should be discarded or reserved for rough work. (Directions for cleaning cells are detailed in Chapter 4).

Generally speaking, trained technicians may operate any of the spectrophotometers successfully. However, interpretation of data from both the UV and IR instruments becomes increasingly complex, and requires more training and specialization. IR interpretation requires special training, and because of the special techniques of sample preparation, instrument operation, and interpretation of absorption curves, mere compliance with the operations manual is not sufficient.

3.6.5. Atomic Absorption

There are a number of differences in the basic design and accessories for atomic absorption equipment that require consideration before purchase and during subsequent use. These choices concern the light source, nebulizer burners, optical systems, readout devices, and mode conversion. Some of these choices are not readily obvious, and require that the purchaser or user be familiar with the types and numbers of samples to be analyzed and the specific elements to be measured before a choice is made. For a program analyzing a wide variety of samples for a number of elements at varying concentrations, an instrument of maximum versatility would be required. A typical atomic absorption unit is shown in Figure 3-6.

3.6.5.1 Lamp Mounts

A basic design feature of atomic absorption spectrometers is the convenience of the hollow cathode (HC) lamp changeover system. Some instruments provide for as many as six lamps in a rotating turret, all electronically stabilized and ready for use by simply rotating the lamp turret. Other instruments provide for use of only one lamp at a time in the lamp housing, and require manual removal and replacement whenever more than one element is to be measured. A quick changeover system is desirable, especially if a number of lamp changes are needed during a period of operation. Conversely, if lamp changes are infrequent, multi-lamp mounts do not represent a great convenience.

For optimal use of the instrument, certain precautions should be observed. After the proper lamp has been selected the hollow cathode current should be adjusted according to the manufacturer's recommendations and allowed to electronically stabilize (warm up) before use. This requires approximately 15 minutes. During this period, the monochromator may be positioned at the correct wavelength and the proper slit width selected. For those instruments employing a multi-lamp turret, a warm-up current is provided to those lamps not in use, thereby minimizing the warm-up period when the turret is rotated. In a single-lamp instrument, the instability exhibited during warm-up is minimized by the use of a double-beam optical system.

3.6.5.1.1 Single Element and Multi-Element Lamps

As an adjunct to single-lamp mounts, HC lamps using from two to as many as six elements in combination are available, thereby increasing the versatility of the AA spectrometer. For instance, a single-lamp instrument such as the Perkin-Elmer may analyze for elements with only one lamp substitution, whereas a six-lamp turret such as the Jarrell-Ash (590 Lincoln Street, Waltham, Mass. 02154), using multi-element lamps could run 18 or more elements.

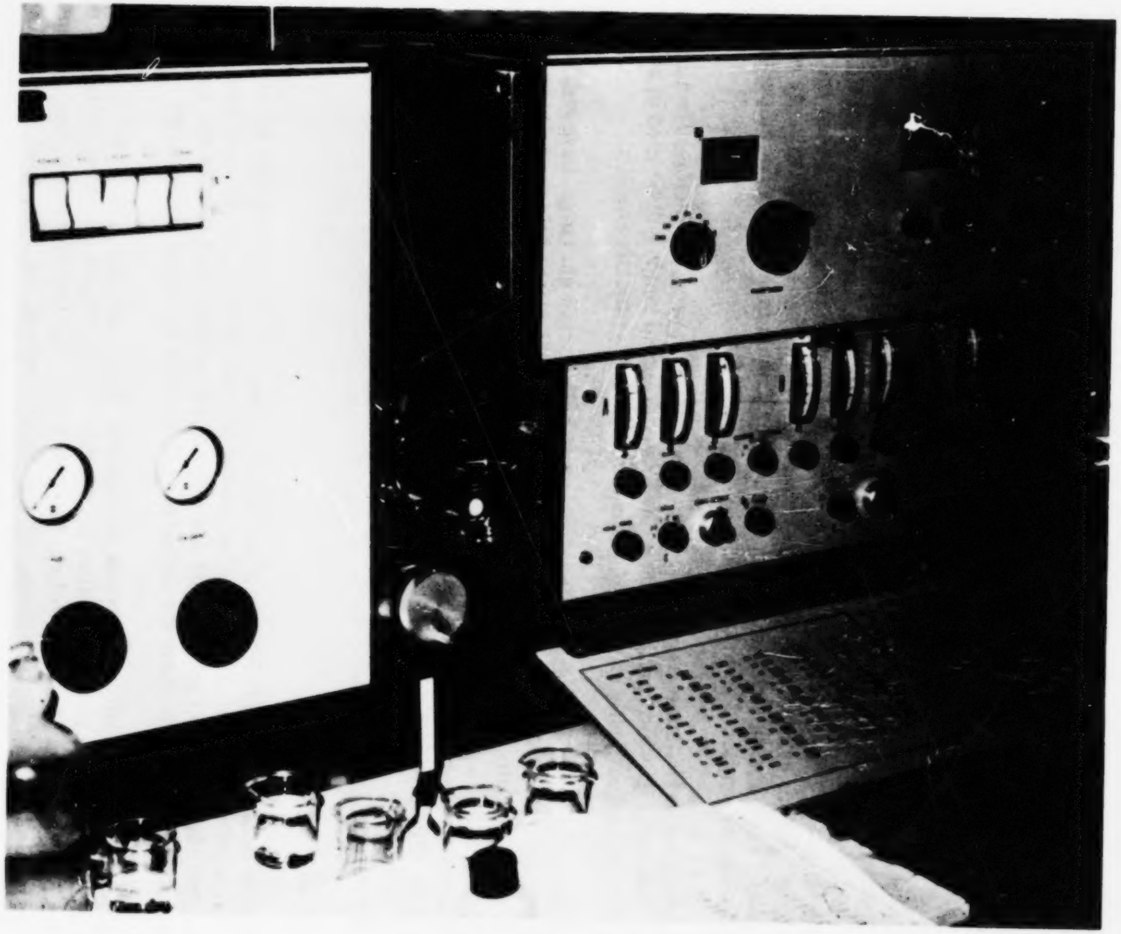

Figure 3-6. ATOMIC ABSORPTION UNIT

Multi-element lamps are considerably cheaper per element than single-element lamps, but the savings may not realized if the lamps are not used strategically, because all the elements in the cathode deteriorate when the lamp is used, regardless of which element is measured. The deterioration phenomena results from the different volatilities of metals used in the cathode. One metal volatilizes (sputters) more rapidly than the others and redeposits upon the cathode causing an increase in surface area of that metal, and decreasing the exposed area of the other cathode metals. Thus, with continual use, a drift in signal will be noted with at least one metal increasing and the other (or others) decreasing. If one can ignore the dubious cost savings of multi-element lamps, use of single-element lamps would result in more precise and accurate data.

The individual line intensities of an element in a multi-element HC lamp will usually be less than that of a lamp containing a pure cathode of the same element. This is because each element must now share the discharge energy with all other elements present. However, this reduction should not affect the output by a factor of more than 1/2 to 1/6, depending on the combination and number of elements combined. The output can be even greater in some multi-element lamps because alloying may permit a higher operating current than the pure cathode itself. All HC lamps have life expectancies which are related to the volatility of the cathode metal, and for this reason, the manufacturer's recommendations for amperage at which the lamp is operated should be closely followed.

A recent advance in HC lamp design, the high-intensity lamp, promises increased sensitivity for some elements. It is also predicted that the newly designed lamps will be used in atomic fluorescence techniques, with significant gains in sensitivity for metals analysis.

Recent improvements in design and manufacture of hollow cathode lamps have resulted in lamps with more constant output and a longer life. Under normal conditions a HC lamp may be expected to operate satisfactorily for several years. At one time, hollow cathode lamps were guaranteed for a minimum amp-hour period. This has been changed, however, to a 90-day warranty. It is good practice to date newly purchased lamps and inspect immediately upon receipt. Operating current and voltage will be indicated on the lamp and should not be exceeded during use. An increase in background noise and/or a loss of sensitivity are signs of lamp deterioration.

3.6.5.2 Burner Types

The most difficult and inefficient step in the AA process is converting the metal in the sample from an ion or a molecule to the neutral atomic state. It is the function of the atomizer and the burner to produce the desired neutral atomic condition of the elements. With minor modifications burners are the same as those used for flame photometry.

Basically there are two different types of burners. They are the total-consumption or surface-mix burner, and the laminar-flow or pre-mix burner. There are many variations of these two basic types, such as the Boling, the high-solids, the turbulent-flow, the tri-flame, nitrous-oxide burner and many others. As one might expect, there are many similarities among the various burners, the different names resulting from the different manufacturers. The element being determined and the type of sample solution dictate the type of burner to be used.

Generally, all types and makes of burners can be adjusted laterally, rotationally and vertically for selection of the most sensitive absorbing area of the flame for the specific element sought. The vertical adjustment is probably the most important since the position of greatest sensitivity varies from element to element.

Burner height is of utmost importance in changing from one element to another. Certain instruments are provided with a vernier adjustment for reproducing burner-height settings, but many are not. Figure 3-7 shows a simply designed device used in the Analytical Quality Control Laboratory for reproducing exact burner height. The gauge is positioned on the burner and the height determined from the light beam striking the calibrated scale. The point at which the beam strikes the gauge is recorded for future use.

3.6.5.3 Single-Beam and Double- (Split) Beam Instruments

There is a great deal of existing uncertainty among instrument users about the relative merits of single-beam and double-beam instruments. Neither system is the final answer.

With a single-beam instrument the light beam from the source passes directly through the flame to the detector. In a double-beam system the light from the source is divided by a beam splitter into two paths. One path, the reference beam, goes directly to the detector. The second path, the sample beam, goes through the flame to the detector. The chopper alternately reflects and passes each beam, creating two equal beams falling alternately upon the detector. If the beams are equal they cancel the alternate impulses reaching the detector and no signal is generated. If the beams are different, the resulting imbalance causes the detector to generate an a.c. signal which is amplified and measured. Any difference between the reference and sample beam is measured as a direct function of absorbed light. The advantage of the double-beam design, therefore, is that any variations in the source are of reduced importance, and smaller dependence is placed upon the stability of the power supply. However, stabilization of the power supply can eliminate the apparent need for the split-beam system. Further, a beam splitter requires use of additional mirrors or optical accessories that cause some loss of radiant energy. Neither system, however, compensates for variation in flame intensity.

A single-beam system does not monitor source variations but offers certain other advantages. It allows use of low-intensity lamps, smaller slit settings and smaller gain. As a consequence, the single-beam instrument, properly designed, is capable of operating with lower noise, better signal-to-noise ratio and therefore better precision and improved sensitivity. Because the simplified optical system conserves radiant energy, especially in the shorter wavelengths, it facilitates operation in the low wavelength range. With this advantage, it should be possible to obtain better sensitivity for those elements with strong resonance lines below 350 $m\mu$ and even those slightly below 300 $m\mu$.

3.6.5.4. Readout Devices

Early models of the AA instrument offered only a meter, calibrated in percentage absorption. In the surge of competitive design, more sophisticated readout devices were built into or offered as accessories to various models. At the present time any desired readout method may be obtained with almost any instrument. Less expensive designs still provide meters with conventional needle indicators. More costly instruments offer any combination of built-in digital scalers, calibrated in concentration, external digital printout in concentration, typewriter printout or typewriter with punch tape. Even inexpensive instruments are built with recorder interfacing.

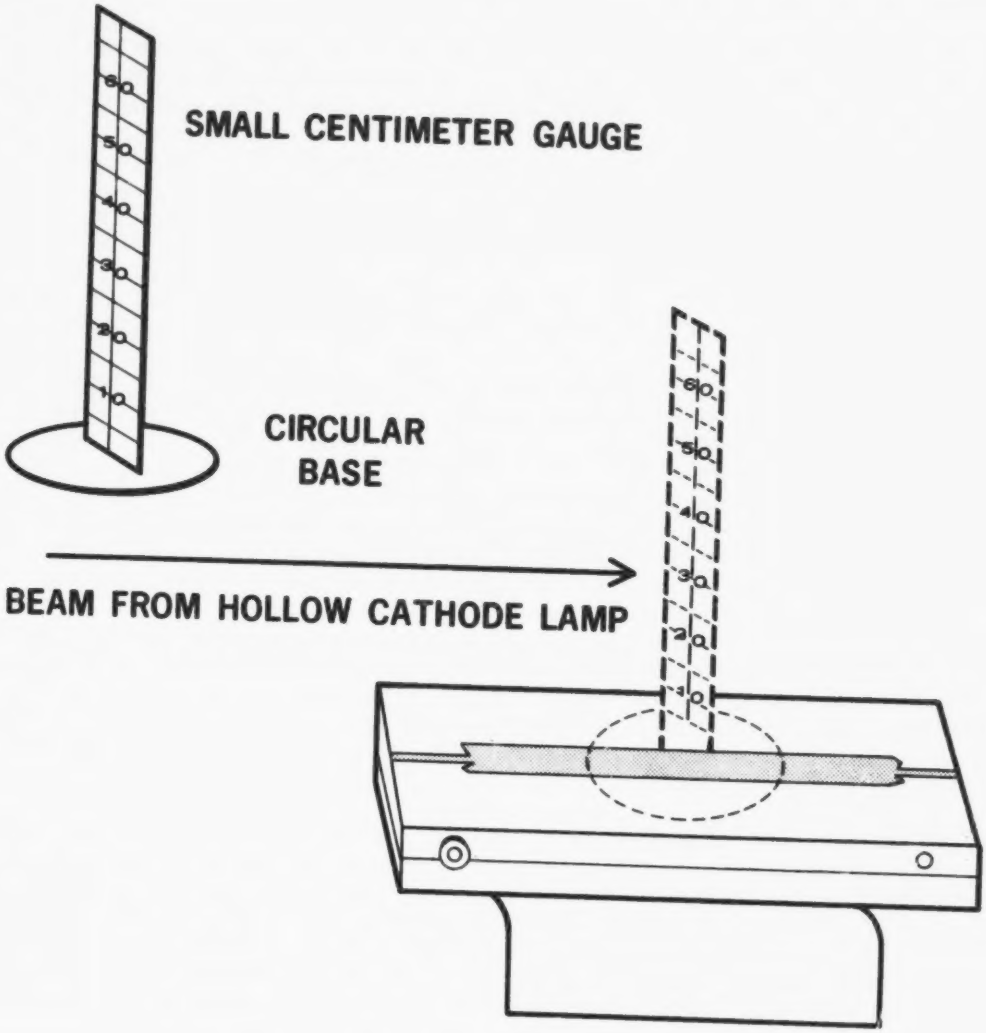
SMALL CENTIMETER GAUGE
CIRCULAR BASE
BEAM FROM HOLLOW CATHODE LAMP
6.0
5.0
4.0
3.0
2.0
1.0

Figure 3-7 DEVICE FOR REPRODUCIBLE POSITIONING OF BURNER HEIGHT

Choice of a readout system is predicated largely upon laboratory needs and availability of budget. In general, any step toward complete automation is desirable but the degree of automation should be compatible with the laboratory program.

3.6.5.5 Miscellaneous Accessories

A number of instruments contain a mode selector, making an instrument usable for either flame absorption or flame emission. The conversion to flame emission is a desirable feature since certain elements are more amenable to analysis by this method.

Automatic sample changers are offered for almost all instruments on the market, and as has been previously stated, any automation feature is desirable. However, unless a laboratory program performs a large number of repetitious measurements daily, an automatic sample changer would not be required. As a practical measure, other commonly used sample-changing devices not expressly designed for AA use, can easily be interfaced with almost any AA instrument.

3.6.5.6 Instrument Choice

Table 3-6 summarizes some of the design features of various commercially available instruments. Since many of the features are common to most models, the basic choice appears to be between double-beam and single-beam instruments. On this basis, at this writing, it is probable that the most widely used instrument in the EPA is the Perkin-Elmer 303, one of two double-beam instruments on the market.

The Instrumentation Laboratories Model 153 (113 Hartwell Ave., Lexington, Mass. 02173) has a number of desirable features. In addition to features listed in the table, it includes push-button ignition, push-button wavelength scan, fail-safe solenoids to prevent improper flame settings, fail-safe flame monitoring, absorption integrator at selected time intervals, visual "peaking" meters, curve correction and several other features. The new Perkin-Elmer Model 403 also offers most of these features in addition to very sophisticated data handling accessories.

3.7 Organic Carbon Analyzer

A number of devices designed to measure the organic content of aqueous samples have appeared on the market within the last five years. The oldest, or first of these instruments, is the Dow Beckman Carbonaceous Analyzer (Figure 3-8). The apparatus measures organic carbon as carbon, by oxidizing a very small sample at a temperature of 900°, in a stream of oxygen, converting all organically bound carbon to carbon dioxide, which is then measured by a Golay-type thermal detector. The instrument is able to detect about 20 mg. of carbon. A recent modification of the original Dow Beckman Carbonaceous Analyzer employs a dual-combustion-tube system operating at different temperatures to distinguish between total carbon and inorganic carbon. Organic carbon is found by difference.

Another such instrument, also developed by Dow Chemical Company, is marketed by the Fisher Scientific Company (Instrument Division, 711 Forbes Ave., Pittsburgh, Pa. 15219) as the "Aquarator". The principle of operation is similar to the Dow Beckman Carbonaceous Analyzer, except that carbon dioxide fed through the combustion tube is reduced to carbon monoxide and measured in an infrared detector. The reaction does not measure carbon, per se, but reducing materials. The results can be equated with the COD test, but the instrument is best suited for industrial wastes and sewage. It lacks the sensitivity needed for COD measurements on relatively clean waters. The lower limit of measurement is about 40 mg/l COD.

A third instrument developed by Dow researchers is franchised to Ionics Corporation (165 Grove Street, Watertown, Mass. 02172) and sold as the "TOD Analyzer". This instrument is also similar in principle to the carbon analyzer, except that the device measures oxygen in and out of the combustion tube. Depletion of oxygen is correlated with oxygen demand of the sample. However, the reaction of oxygen with sulfur and nitrogen is not stoichiometric, and results for some samples may be questionable. A malfunction of the sample injection system appears to be the main problem with the instrument to date. An evaluation study conducted by the Hudson Delaware Basins Office, EPA, indicates a very good potential use for the instrument.

Another device, designed by Union Carbide Corporation (Ionics Inc., 65 Grove St., Watertown, Mass. 02172) is similar to the original Dow Beckman Analyzer except that the combustion tube contains a coil of heated palladium wire. An aqueous sample injected into the combustion tube is decomposed to hydrogen and oxygen through the catalytic action of the palladium. Carbon from organic matter combines with the water-produced oxygen to form carbon dioxide, with a final infrared measurement. Results obtained are theoretically identical to the Dow Beckman Analyzer, but the repeated failure of the sample injection system has prevented evaluation of the apparatus as a laboratory instrument. It is being routinely used, however, as a continuous monitoring system for total carbon.

To date the only instrument which has been successfully demonstrated and which meets the needs of EPA laboratories is the Dow Beckman Carbonaceous Analyzer or its successor, the Model 915. Operating instructions for this device are detailed elsewhere (4).

Precautions to be observed in use of the Dow Beckman Carbonaceous Analyzer or the DB Model 915 are detailed below:

a. All inorganic carbon present in the sample as carbonate or bicarbonate must be removed prior to analysis, or accounted for, when using the Model 915.

b. Particulate matter in the sample should not be larger than the opening of the hypodermic needle used to take the sample. If necessary the sample should be homogenized by some means designed to reduce the particle size.

c. The instrument should be preconditioned with repeated injections of distilled water to obtain stable operating conditions before actual sample injection.

d. Furnace temperature and oxygen flow should be maintained at proper settings during period of operation.

e. Perform periodic maintenance of instrument as follows:

   1. repack combustion tube with fresh asbestos,
   2. clean and dry micro filter,
   3. clean and dry infrared cell,
   4. recharge reference cell with nitrogen.

Need for replacement of asbestos packing is indicated by a loss of sensitivity and wide

Table 3-6.

DESIGN FEATURES OF SOME COMMON ATOMIC ABSORPTION INSTRUMENTS

Design Feature	Inst. Labs	Jarrell-Ash	Norelco-Unicam	Perkin-Elmer	Varian	Hewlett-Packard	Bausch & Lomb	Beckman
Model Number	153	82-500	SP-90	403	AA4	5960 A	AC2-20	979
Source Arrangement	Turret-6	Turret-6	Turret-3	Single Lamp	Turret-4	Turret-6	Turret-3	Turret-3
Optical System	Dual double-beam, beam, grating, single pass	Single-beam, a.c., grating, multipass	Single-beam a.c., prism	Double-beam, grating	Single-beam, grating	Single-beam, a.c., interference filter	Single-beam, a.c., grating, single-pass	Single-beam, grating, multipass
Mode	Absorption and emission	Absorption and emission	Absorption and emission	Absorption and emission	Absorption and emission	Absorption only	Absorption and emission plus UV visible spectrophotometry	Absorption, emission, and regular spectrophotometric analysis
Detector	Photomultiplier	Photomultiplier	Photomultiplier	Photomultiplier	Photomultiplier	Photomultiplier	Photomultiplier	Photomultiplier
Detector Substitution	Yes–Photodiode in Channel B	Yes	Yes	--	Yes	Not given	Not given	Not given
Readout	Direct concentrational readout with curve corrector	Meter readout plug-in recorder	Meter readout or recorder	Digital concentration readout	Meter readout	Meter readout	Meter readout	Meter–plug-in recorder
Range	190-800 mμ	190-800 mμ	190-770 mμ 198-850 with special photo tube	190-800 mμ	--	190-800 mμ	190-800 mμ	190-770 mμ, 190-852 mμ optional
Slit	Adjustable	Adjustable	Adjustable	Adjustable	Adjustable	Fixed	Adjustable and fixed	Adjustable
Accessories	Data printer, sample changer, curve correction	Digital concentration readout, sample changer	Plug-in electronics, automatic sample changer with log recorder	Typewriter readout, sample changer	Digital printer with curve correction, sample changer	Recorder readout	Recorder readout, B&L concentrational readout, sample changer	Digital readout, data printer, sample changer
Special	2 elements simultaneously using interference filters, push button operation	5-pass system	plug-in electronics	Paper punch tape with typewriter to produce a typed report, push button operation	186-1000 mμ	Push-button operation for one of six preset determinations	Dialable filters for work above 560 mμ	3-pass system

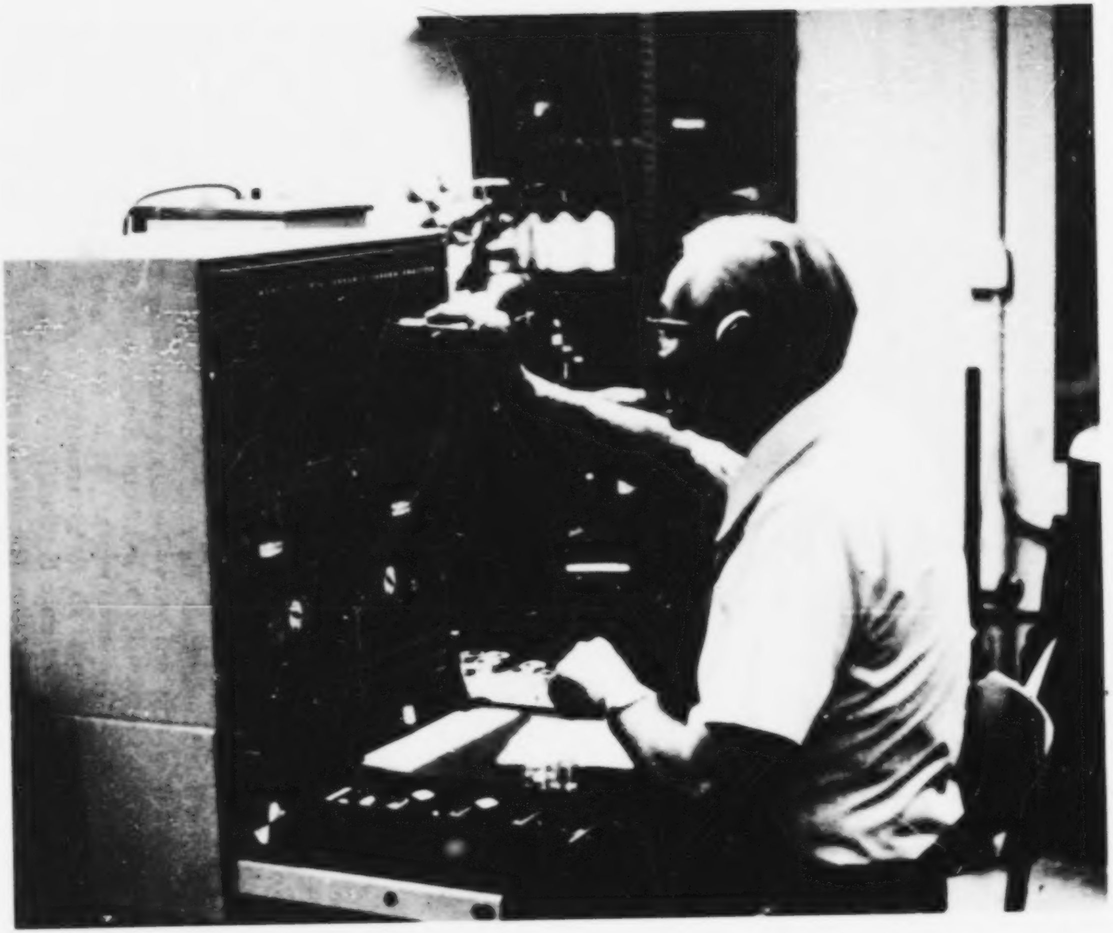

Figure 3-8. ORGANIC CARBON ANALYZER

peaks. Unsteady baseline and excessive noise is caused by a dirty or partly clogged micro filter. An accumulation of moisture in the infrared cell is indicated by loss of sensitivity and excessive noise.

3.8 Selective Ion Electrodes

In recent years a variety of ion-selective electrodes have been commercially available, and show great promise as fast and efficient tools for in situ monitoring and for laboratory analysis of all types of samples. A list of ions susceptible to analysis is indicative of the interest and progress being made in this field. Electrodes, or "probes" as they are popularly called, are available for measurement of monovalent cations, sulfate, nitrate, perchlorate, and a number of others. Dissolved oxygen probes should also be included in this list, although they are not technically selective ion probes. There have been a number of reviews concerning the theory and application of probes, most recently a concise article by Rechnitz (5).

Selective ion probes generally measure what they claim to measure–specific ion activity. They do not measure concentrations of un-ionized materials. For example, the probe designed to measure divalent cations promises to measure total hardness as a function of calcium and magnesium. However, since the probe does not respond to un-ionized calcium and magnesium, it does not accurately measure total hardness. As a consequence of this deficiency, much investigation is being carried out to devise means of determining total concentration of the constituent sought.

"Methods for Chemical Analysis of Water and Wastes" (4) outlined procedures for use of two probes, fluoride and DO. The chloride probe is also used on the automatic monitoring devices and will be listed as an approved procedure in future editions of EPA Methods. Evaluation of additional ion selective electrodes for cyanide, ammonium, and sulfide ions is now underway, and will be reported in the near future. Various techniques for use of the probes are reviewed by Riseman (6).

Personnel in water pollution laboratories are encouraged to investigate the use of selective ion probes as a means of reducing analytical work and improving data quality. At the present time, however, only the fluoride, DO, and chloride probes are recommended for routine use in data collection.

A basic question relating to the use of selective ion probes is the number of standards required to prepare a standard curve. It is generally agreed that the more standards used for the preparation of a colorimetric curve, the more reliable the data resulting from use of the curve. On the other hand, only one or two points are normally used in standardization of a meter for measuring pH, conductivity or DO. In the conversion of a colorimetric procedure such as fluoride to a probe-type measurement, the tendency is to prepare a millivolt vs concentration curve using the usual six to ten standards. Probe manufacturers insist that only one or two points are needed since the linearity of response has been established and only the slope of the line must be known. The alternatives are:

a. Take readings in distilled water at 0 and at some concentration approximating concentration of sample; establish slope of line.

b. Take readings in distilled water at 0 and two concentrations bracketing expected concentration of unknowns to establish curve or slope.

c. Take readings at 0 and at decade concentrations as 1, 10, 100, etc., for standard curve.

d. Take reading of sample, add known increment of measured constituent and read again; establish proportionality factor.

The method for the use of the fluoride electrode specifies use of multiple standards in the range between 0 to 2 mg/liter, because this system has supplied very precise data when compared to the colorimetric methods using the same set of standards. The system of incremental addition appears to have considerable merit since the electrode response is established in the presence of possible interferences. At the present time no single procedure for standardizing probe response has been adopted by a majority of users.

When a selective ion electrode appears to be malfunctioning, the same check system may be used as for a faulty glass pH electrode. It is unlikely, however, that the electrode will be cracked; it will probably be dry, or insufficiently filled with the necessary solution. The probe assembly and instructions for refilling customarily accompany the item when shipped by the manufacturer and said instructions should be followed by the user.

Selective ion probes are available from several manufacturers including Beekman, Corning, Coleman and Orion. The Orion organization (11 Blackstone St., Cambridge, Mass. 02139) is the largest producer in the field and offers not only selective ion probes but a sizable complement of electronic equipment for use with the probes. Figure 3-9 illustrates an Orion selective ion meter.

Dissolved oxygen probes and meters of various designs have been offered by a large number of manufacturers including Weston & Stack, Beckman, Jarrell-Ash, Union Carbide, Yellow Springs Instrument, Delta Scientific, and others.

3.9 References

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2. 1968 Book of ASTM Standards, Part 23; Test for pH of Industrial Waste Water, pp. 292-3; American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103.
3. Black, A. P., and Hannah, S. A., "Measurement of Low Turbidities," JAWWA, 57, 901 (1965).
4. Methods for Chemical Analysis of Water and Wastes, EPA, Analytical Quality Control Laboratory, 1971.
5. Rechnitz, G. A., "Ion Selective Electrodes," Chemical Engineering News, p. 146, June 12, 1967.
6. Riseman, Jean M., "Measurement of Inorganic Water Pollutants by Specific Ion Electrode," American Laboratory, p. 32, July 1969.

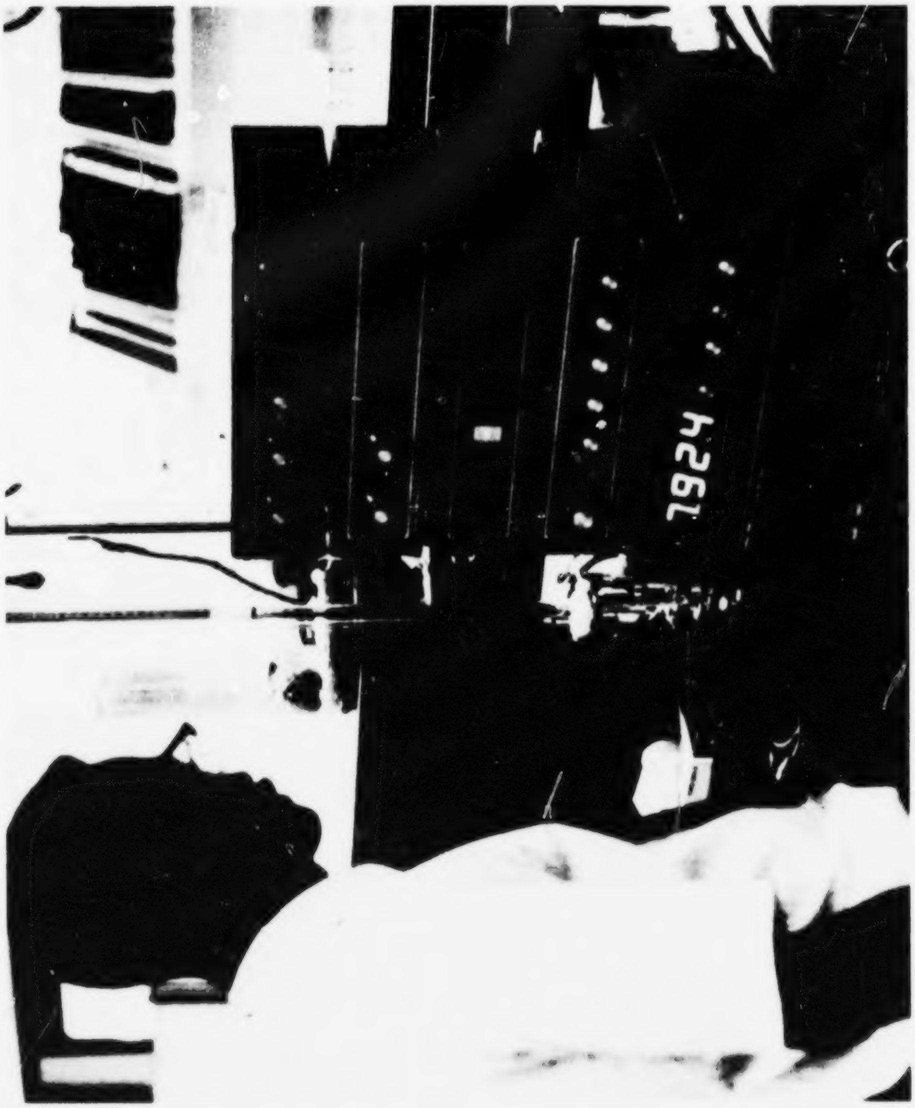


Figure 3-9. SELECTIVE ION METER

CHAPTER 4

GLASSWARE

4.1 General

The measurement of trace constituents in water demands methods capable of maximum sensitivity. This is especially true for metals and trace organics such as pesticides, as well as for the determination of ammonia and phosphorus. In addition to sensitive methods, however, there are other areas that require special consideration. One such area is that of the cleanliness of laboratory glassware. Obviously, the very sensitive analytical systems are more sensitive to errors resulting from the improper use or choice of apparatus, as well as to contamination effects due to an improper method of cleaning the apparatus. The purpose of this chapter is to discuss the kinds of glassware available, the use of volumetric ware, and various cleaning requirements.

4.2 Types of Glassware

Laboratory vessels serve three functions: storage of reagents, measurement of solution volumes and confinement of reactions. For special purposes, vessels made from materials such as porcelain, nickel, iron, aluminum, platinum, stainless steel, and plastic may be employed to advantage. Glass, however, is the most widely used material of construction. There are many grades and types of glassware from which to choose, ranging from student grade to others possessing specific properties such as resistance to thermal shock, alkali, low boron content, and super strength. Soft-glass containers are usually relatively soluble, and therefore are not recommended for general use, especially for storage of reagents. The mainstay of the modern analytical laboratory is a highly resistant borosilicate glass, such as that manufactured by Corning Glass Works under the name "Pyrex" or by Kimble Glass Co. as "Kimax". This glassware is satisfactory for all analyses included in "Methods for Chemical Analysis of Water and Wastes (1)."

Depending on the particular manufacturer, various trade names are used for specific brands possessing special properties such as resistance to heat, shock, alkalies, etc. Examples of some of these follow:

a. Kimax- or Pyrex-brand glass is a relatively inert all-purpose borosilicate glass.

b. Vycor-brand glass is a silica glass (96%) made to withstand continuous temperatures up to 900°C and can be down-shocked in ice water without breakage.

c. Corning brand glass is claimed to be 50 times more resistant to alkalies than conventional ware and practically boron free (max. 0.2%).

d. Ray-Sorb- or Low-Actinic-brand glass is for use with light-sensitive material.

e. Corex-brand labware is harder than conventional borosilicates, better able to resist clouding and scratching.

The use of plastic vessels, containers and other apparatus made of Teflon, polyethylene, polystyrene and polyproplylene has increased markedly over recent years. Some of these materials, such as Teflon, are quite expensive; however, Teflon stopcock plugs have practically replaced glass plugs in burets, separatory funnels, etc. because lubrication to avoid sticking or "freezing" is not required. Polyprolylene, a methylpentene polymer, is available as laboratory bottles, graduates, beakers and even volumetric flasks. It is crystal clear, shatter-proof, autoclavable and chemically resistant.

Some points to consider in choosing glassware and/or plasticware are:

a. Generally, the special types of glass listed above are not required to perform the analyses given in "Methods for Chemical Analysis of Water and Wastes" (1).

b. Unless instructed otherwise, borosilicate or polyethylene bottles are to be used for the storage of reagents and standard solutions.

c. Certain dilute metal solutions may plate out on glass container walls over long periods of storage. Thus, dilute metal standard solutions are prepared fresh at the time of analysis.

d. For some operations, disposable glassware is entirely satisfactory. One example is the use of disposable test tubes as sample containers for use with the Technicon Automatic Sampler.

e. Plastic bottles of polyethylene and/or Teflon have been found satisfactory for the shipment of water samples. Strong mineral acids (such as sulfuric acid) and organic solvents will readily attack polyethylene and are to be avoided.

f. Borosilicate glassware is not completely inert, particularly to alkalies; therefore, standard solutions of silica, boron and the alkali metals are usually stored in polyethylene bottles.

For additional information the reader is referred to the catalogs of the various glass and plastic manufacturers. These catalogs contain a wealth of information as to specific properties, uses, sizes, etc.

4.3 Volumetric Analyses

By common usage, accurately calibrated glassware for precise measurements of volume has become known as volumetric glassware. This group includes volumetric flasks, volumetric pipets and accurately calibrated burets. Less accurate types of glassware including graduated cylinders, serological and measuring pipets also have specific uses in the analytical laboratory, when exact volumes are unnecessary. A typical laboratory glassware setup is shown in Figure 4-1.

The precision of volumetric work depends in part upon the accuracy with which volumes of solutions can be measured and there are certain sources of error which must be carefully considered. The volumetric apparatus must be read correctly; that is, the bottom of the meniscus should be tangent to the calibration mark. There are other sources of error, however, such as changes in temperature which result in changes in the actual capacity of glass apparatus and in the volume of the solutions.The capacity of an ordinary glass flask of 1000 ml volume increases 0.025 ml per degree rise in temperature, but if made of borosilicate glass the increase is much less. One thousand ml of water or of most 0.1 N solutions increases in volume by approximately 0.20 ml per 1°C increase at room

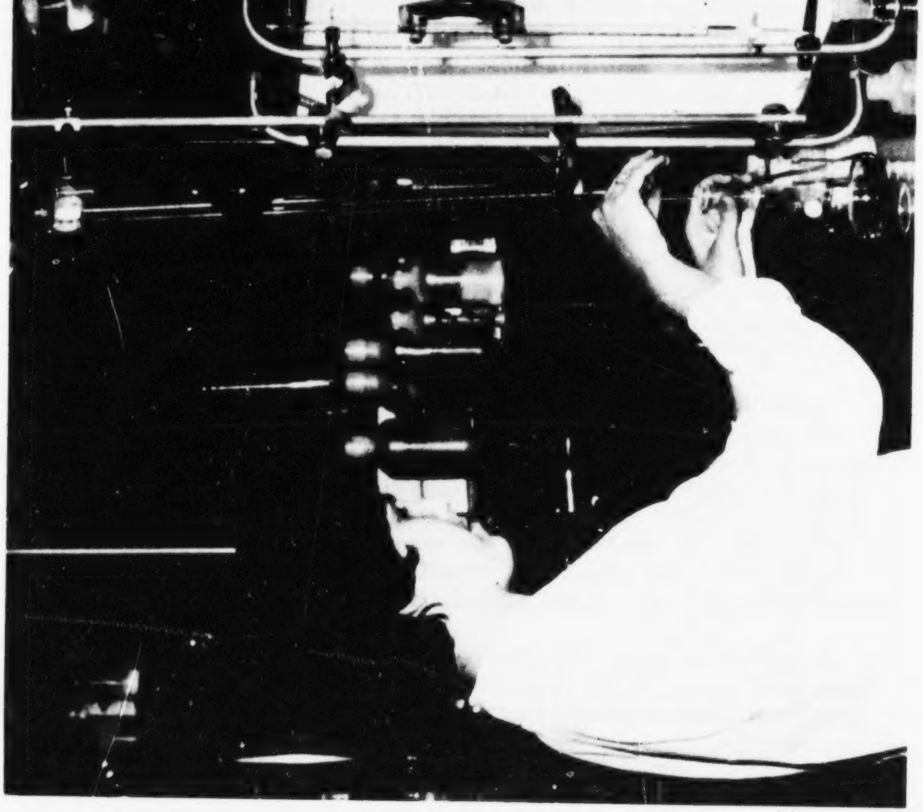


Figure 4-1. TITRATION BENCH

temperature. Thus solutions must be measured at the temperature at which the apparatus was calibrated. This temperature (usually 20°C) will be indicated on all volumetric ware. There may also be errors of calibration of the apparatus; that is, the volume marked on the apparatus may not be the true volume. Such errors can be eliminated only by recalibrating the apparatus or by replacing it.

Volumetric apparatus is calibrated "to contain" or "to deliver" a definite volume of liquid. This will be indicated on the apparatus with the letters "TC" (to contain) or "TD" (to deliver). Volumetric flasks are calibrated to contain a given volume. They are available in various shapes and sizes ranging from 1- to 2000-ml capacity.

Volumetric pipets are calibrated to deliver a fixed volume. The usual capacities are 1 thru 100 ml although micro-pipets are also available. In emptying volumetric pipets, they should be held in a vertical position and the outflow should be unrestricted. The tip of the pipet is kept in contact with the wall of the receiving vessel for a second or two after the free flow has stopped. The liquid remaining in the tip is not removed; this is most important.

Measuring and serological pipets should also be held in a vertical position for dispensing liquids; however, the tip of the pipet is only touched to the wet surface of the receiving vessel after the outflow has ceased. For those pipets where the small amount of liquid remaining in the tip is to be blown out and added, indication is made by a frosted band near the top. The band is usually located far enough down so that it will not touch the technician's lips when liquid is being drawn up or blown out.

Burets are used to deliver definite volumes. The more common types are usually of 25- or 50-ml capacity, graduated to tenths of a milliliter, and are provided with stopcocks. For precise analytical methods in microchemistry, micro-burets are also used. Micro-burets generally are of 5- or 10-ml capacity, graduated in hundredths of a milliliter division. Automatic burets with reservoirs are also available ranging in capacity from 10 to 100 ml. Reservoir capacity ranges from 100 to 4000 ml.

General rules in regard to the manipulation of a buret are as follows: Do not attempt to dry a buret which has been cleaned for use, but rinse it two or three times with a small volume of the solution with which it is to be filled. Do not allow alkaline solutions to stand in a buret, because the glass will be attacked, and the stopcock, unless made of Teflon, will tend to freeze. A 50-ml buret should not be emptied faster than 0.7 ml per second, otherwise too much liquid will adhere to the walls and as the solution drains down, the meniscus will gradually rise, giving a high false reading. It should be emphasized that improper use of and/or reading of burets can result in serious calculation errors.

In the case of all apparatus for delivering liquids, the glass must be absolutely clean so that the film of liquid never breaks at any point. Careful attention must be paid to this fact or the required amount of solution will not be delivered. The various cleaning agents and their use are described later.

4.4 Federal Specifications for Volumetric Glassware

Circular 602 of the National Bureau of Standards, "Testing of Glass Volumetric Apparatus", describes the Federal Specifications for volumetric glassware. The National Bureau of Standards no longer accepts stock quantities of volumetric apparatus from manufacturers or dealers for certification and return for future sale to consumers. This certification service is still available, but apparatus will be tested only when submitted by the ultimate user, and then only after an agreement has been reached with the Bureau concerning the work to be done.

Consequently, the various glass manufacturers have discontinued the listing of NBS-certified ware. In its place catalogue listings of volumetric glass apparatus which meet the Federal Specifications are designated as Class A and all such glassware is permanently marked with a large "A". These NBS specifications are listed in Table 4-1. The ware in question includes the usual burets, volumetric flasks and volumetric pipets.

Table 4-1

TOLERANCES FOR VOLUMETRIC GLASSWARE
(Abridged from National Bureau of Standards Data, 1941)

Capacity (ml) less than and including	Limit of error (ml)
Graduated Flasks	
25	0.03
50	0.05
100	0.08
200	0.10
250	0.11
300	0.12
500	0.15
1,000	0.30
2,000	0.50
Transfer pipets	
2	0.006
5	0.01
10	0.02
25	0.025
30	0.03
50	0.05
100	0.08
200	0.10
Burets[1]	
5	0.01
10	0.02
30	0.03
50	0.05
100	0.10

---

[1] *Limits of error are of total or partial capacity. Customary practice is to test the capacity at 5 intervals.*

In addition to the "A" marking found on calibrated glassware and the temperature at which the calibration was made, other markings also appear. These include the type of glass, such as Pyrex, Corex, Kimax, etc., the stock number of the particular item, and the capacity of the vessel. If the vessel contains a ground-glass connection, this will also be included along with the TD or TC symbol. An example of the markings usually found on volumetric ware is shown in Figure 4-2.

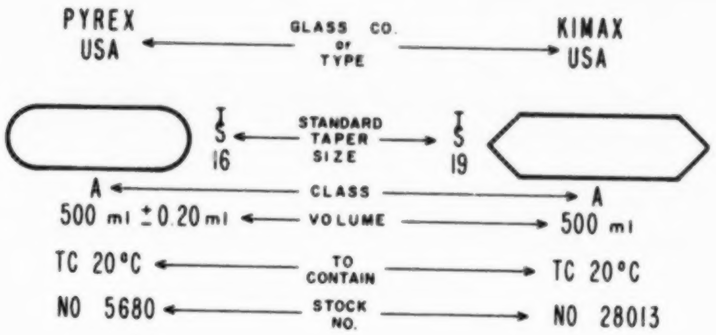


Figure 4-2. EXAMPLE OF MARKINGS ON GLASSWARE

Class A glassware need not be recalibrated before use. However, if it should become necessary to calibrate a particular piece of glassware, directions may be found in texts (2) on quantitative analysis.

4.5 Cleaning of Glass and Porcelain

The method of cleaning should be adapted to both the substances that are to be removed, and the determination to be performed. Water-soluble substances are simply washed out with hot or cold water, and the vessel is finally rinsed with successive small amounts of distilled water. Other substances more difficult to remove may require the use of a detergent, organic solvent, dichromate cleaning solution, nitric acid or aqua regia (25 percent v/v conc. HNO_3 in conc. HCl). In all cases it is good practice to rinse a vessel with tap water as soon as possible after use. Material allowed to dry on glassware is much more difficult to remove.

Volumetric glassware, especially burets, may be thoroughly cleaned by a mixture containing the following: 30 g sodium hydroxide, 4 g sodium hexametaphosphate (trade name, Calgon), 8 g trisodium phosphate, and 1 liter water. A gram or two of sodium lauryl sulfate or other surfactant will improve its action in some cases. This solution should be used with a buret brush.

Dichromate cleaning solution (chromic acid) is a powerful cleaning agent; however, due to its destructive nature upon clothing and upon laboratory furniture, extreme care must be taken when using this mixture. If any of the solution is spilled, it must be cleaned up immediately. Chromic acid solution may be prepared in the laboratory by adding 1 liter of concentrated sulfuric acid slowly, with stirring, to 35 ml saturated sodium dichromate solution. This mixture must be allowed to stand for approximately 15 minutes in the vessel which is being cleaned and may then be returned to a storage bottle. Following the chromic-acid wash, the vessels are rinsed thoroughly with tap water, then with small successive portions of distilled water. Fuming nitric acid acts more rapidly, but is disagreeable to handle. In either case, when the acid becomes dilute, the cleaning mixture is no longer effective. A mixture of concentrated sulfuric and fuming nitric acids is even more efficient but is also hazardous to use. A persistent greasy layer or spot may be removed by acetone or by allowing a warm solution of sodium hydroxide, about 1 g per 50 ml of water, to stand in the vessel for 10-15 minutes; after rinsing with water, dilute hydrochloric acid, and water again, the vessel is usually clean. Alcoholic potassium hydroxide is also effective in removing grease. To dry glass apparatus, rinse with acetone and blow or draw air through it.

4.6 Special Cleaning Requirements

Absorption cells, used in spectrophotometers, should be kept scrupulously clean, free of scratches, fingerprints, smudges and evaporated film residues. The cells may be cleaned with detergent solutions for removal of organic residues, but should not be soaked for prolonged periods in caustic solutions because of the possibility of etching. Organic solvents may be used to rinse cells in which organic materials have been used. Nitric acid rinses are permissible, but dichromate solutions are not recommended because of the adsorptive properties of dichromate on glass. Rinsing and drying of cells with alcohol or acetone before storage is a preferred practice. Matched cells should be checked to see that they are equivalent by placing portions of the same solution in both cells and taking several readings of the transmittance (%T) or optical density (OD) values. If a cell is mismatched it should be discarded or reserved for rough work.

For certain determinations, especially trace metals, the glassware should also be rinsed with a 1:1 nitric acid-water mixture. This operation is followed by thoroughly rinsing with tap water and successive portions of distilled water. This may require as many as 12-15 rinses, especially if chromium is being determined. The nitric acid rinse is also especially important if lead is being determined.

Glassware to be used for phosphate determinations should not be washed with detergents containing phosphates. This glassware must be thoroughly rinsed with tap water and distilled water. For ammonia and Kjeldahl nitrogen, the glassware must be rinsed with ammonia-free water (See Chapter 2).

Glassware to be used in the determination of trace organic constituents in water, such as chlorinated pesticides, should be as free as possible of organic contaminants. A chromic acid wash of at least 15 minutes is necessary to destroy these organic residues. Rinse thoroughly with tap water, and finally with distilled water. Glassware may be dried for immediate use by rinsing with redistilled acetone. Otherwise glassware may be oven dried or drip dried. Glassware should be stored immediately after drying to prevent any accumulation of dust. Store inverted or with mouth of glassware covered with foil.

Bottles to be used for the collection of samples for organic analyses should be rinsed successively with chromic acid cleaning solution, tap water, distilled water, and finally several times with redistilled solvent (e.g., acetone, hexane, petroleum ether, chloroform).

Caps are washed with detergent, rinsed with tap water, distilled water and solvent. Liners are treated in the same way as the bottles and are stored in a sealed container.

4.7 Disposable Glassware

When the risk of washing a pipet for reuse becomes too great, as in the case of use with toxic materials, or when the cost of washing glassware becomes prohibitive, disposable pipets may be the answer, provided they meet the necessary specification. Various types are available including bacteriological, serological and micro-dilution pipets. Disposable glassware generally is made of soft glass.

4.8 Specialized Glassware

The use of vessels and glassware fitted with standard-taper, ground-glass, and ball-and-socket joints has increased because of certain advantages such as less leakage and fewer freezeups. Standard-taper, interchangeable ground joints save time and trouble in assembling apparatus. They are precision-ground with tested abrasives to insure an accurate fit and freedom from leakage. Ball and socket joints increase flexibility of operation and eliminate the need for exact alignments of apparatus. Symbols and their meaning as applied to standard joints, stoppers and stopcocks are shown below.

4.8.1. Standard Taper ($\overset{T}{S}$)

$\overset{T}{S}$ is the symbol used to designate interchangeable joints, stoppers and stopcocks, complying with the requirements of Commercial Standard CS-21, published by the National Bureau of Standards. All mating parts are finished to a 1:10 taper.

The size of a particular piece appears after the appropriate symbol. Due primarily to the greater variety of apparatus equipped with $\overset{T}{S}$ fittings, a number of different types of identifications are used, as follows:

a. For joints–a two-part number, as $\overset{T}{S}$ 24/40, with 24 being the approximate diameter in mm at the large end of the taper, and 40 the axial length of taper, also in mm.

b. For stopcocks–a single number, as $\overset{T}{S}$ 2, with 2 mm being the approximate diameter of the hole or holes through the plug.

c. For bottles–a single number, as $\overset{T}{S}$ 19, with 19 mm being the appropriate diameter at top of neck. However, there are differences in dimensions between the bottle and flask stoppers.

d. For flasks, etc. – a single number, as $\overset{T}{S}$ 19, with 19 mm being the appropriate diameter of the opening at top of neck.

4.8.2 Spherical Joints (§)

§ is the designation for spherical (semi-ball) joints complying with CS-21. The complete designation of a spherical joint also consists of a two-part number, as 12/2, with 12 being the approximate diameter of the ball and 2 the bore of the ball and the socket, also in mm.

4.8.3 Product Standard ($\overset{P}{S}$)

$\overset{P}{S}$ is a new symbol. It will appear in a forthcoming NBS Product Standard for stopcocks with Teflon plugs, with the mating surfaces being finished to a 1:5 taper. As with $\overset{T}{S}$ stopcocks, a single number is used. Thus, $\overset{P}{S}$ 2 means a Teflon stopcock with a hole of approximately 2-mm diameter in the plug.

4.9 Fritted Ware

For certain laboratory operations the use of Fritted Ware for filtration (as in total dissolved solids and suspended solids determinations), gas dispersion, absorption, and/or extractions may be of an advantage.

There are six different porosities of Fritted Ware available, so that precipitates varying in size can be filtered at maximum speed with no sacrifice or retentivity. Porosity is controlled in manufacture, and discs are individually tested and graded into these classifications. The extra-coarse and coarse porosities are held toward the maximum pore diameter as listed. The medium, fine, very fine, and ultra-fine are held toward the minimum pore diameter as listed in Table 4-2.

Table 4-2

FRITTED WARE POROSITY

Porosity Grade	Designation	Pore Size (Microns)	Principal Uses
Extra Coarse	EC	17[illegible]220	Coarse filtration. Gas dispersion, washing, absorption.
Coarse	C	40-60	Coarse filtration. Gas dispersion, washing, absorption.
Medium	M	10-15	Filtration and extraction.
Fine	F	4-5.5	Filtration and extraction.
Very Fine	VF	2-2.5	General bacterial filtration.
Ultra-Fine	UF	0.9-1.4	General bacterial filtration.

Pore sizes are determined by the method specified in ASTM E 128, "Maximum Pore Diameter and Permeability of Rigid Porous Filters for Laboratory Use." (3)

4.9.1 Recommended Procedures for Maximum Filter Life

a. New Filters. Wash new filters by suction with hot hydrochloric acid, followed by a water rinse.

b. Pressure Limits. The maximum safe differential pressure on a disc is 15 pounds per square inch.

c. Thermal Shock. Fritted ware has less resistance to thermal shock than non-porous glassware. Hence, excessive, rapid temperature changes and direct exposure to a flame should be avoided. Heating in a furnace to 500°C may be done safely, provided the heating and cooling are gradual. Dry ware may be brought to constant weight by heating at 105-110°C.

Never subject a damp filter of ultra-fine porosity to a sudden temperature change. Steam produced in the interior may cause cracking.

4.9.2 Cleaning of Used Filters

In many cases, precipitates can be removed by rinsing with water, passed through from the underside, with the pressure not exceeding 15 pounds per square inch. The suggestions that follow in Table 4-3 will be helpful in dealing with material that will not be removed by the reverse water-wash. The use of strong alkalies, strong hydrofluoric acid and phosphoric acid should be avoided. Also, scratching of the surfaces will weaken the discs.

Table 4-3

CLEANING OF FILTERS

Material	Removal Agent
Albumen	Hot ammonia or hydrochloric acid
Aluminous and siliceous residues	2% Hydrofluoric acid followed by concentrated sulfuric acid. Rinse immediately with water until no trace of acid can be detected.
Copper or iron oxides	Hot hydrochloric acid plus potassium chlorate.
Fatty materials	Carbon tetrachloride
Mercuric sulfide	Hot aqua regia
Organic matter	Hot concentrated cleaning solution, or hot concentrated sulfuric acid with a few drops of sodium nitrite.
Silver chloride	Ammonium or sodium hyposulfite.

4.10 References

1. "Methods for Chemical Analysis of Water and Wastes," EPA, Analytical Quality Control Laboratory, 1971.

2. Willare, H. H., and Furman, N. H., Elementary Quantitative Analysis–Theory and Practice, D. Van Nostrand Co., Inc., New York (1947).

3. 1968 Book of ASTM Standards, Part 30, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103.

Chapter 5

REAGENTS, SOLVENTS, AND GASES

5.1 Introduction

The objective of this chapter is to provide general information and suggestions that will serve to keep the analyst conscious of his responsibilities in analytical quality control, as they relate to reagents, solvents and gases. While the material presented here will assist the analyst in producing high quality data, it is by no means complete. It is incumbent on the analyst to obtain details of special precautions required to insure proper selection, preparation, and storage of reagents, solvents and gases from the descriptions of individual methods.

5.2 Reagent Quality

Chemical reagents, solvents, and gases are available in a wide variety of grades of purity, ranging from technical grade to various "ultra pure" grades. The purity of these materials required in analytical chemistry varies with the type of analysis. The parameter being measured and the sensitivity and specificity of the detection system are important factors in determining the purity of the reagents required. For many analyses, e.g., most inorganic analyses, analytical reagent grade is satisfactory. Other analyses, e.g., trace organic and radiological, frequently require special "ultra pure" reagents, solvents, and gases. In methods where the purity of reagents is not specified it is intended that analytical reagent grade be used. Reagents of lesser purity than that specified by the method should not be used. The labels on the container should be checked and the contents examined to verify that the purity of the reagents meets the needs of the particular method involved. The quality of reagents, solvents, and gases required for the various classes of analyses: inorganic, metals, radiological, and organic, are discussed below.

Reagents must always be prepared and standardized with the utmost of care and technique, against reliable primary standards. They must be restandardized or prepared fresh as often as required by their stability. Stock and working standard solutions must be checked regularly for signs of deterioration, e.g., discoloration, formation of precipitates, and concentration. Standard solutions should be properly labeled as to compound, concentration, solvent, date, and preparer.

Primary standards must be obtained from a reliable source, pretreated, e.g., dried, under specified conditions, accurately prepared in calibrated volumetric glassware, and stored in containers that will not alter the reagent. A large number of primary standards are available from the National Bureau of Standards (NBS). A complete listing of available standards is given in NBS Special Publication 260 (1). Primary standards may also be obtained from many chemical supply companies. Suppliers for special quality reagents, solvents, and gases are noted in later discussions of the various classes of analyses. Reagents and solvents of all grades are available from many chemical supply houses.

There is some confusion among chemists as to the definition of the terms ANALYTICAL REAGENT GRADE, REAGENT GRADE, and ACS ANALYTICAL REAGENT GRADE. A review of the literature and chemical supply catalogs indicates that the three terms are synonymous. Hereafter, in this document, the term ANALYTICAL REAGENT GRADE

(AR) will be used. It is intended that AR chemicals and solvents shall conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society (2).

The ASTM Manual on Industrial Water and Industrial Waste Water (3), Part 23 of ASTM Standards (4), and "Standard Methods for the Examination of Water and Wastewater" (5) devote separate chapters to problems related to preparation, standardization, and storage of reagents. The information provided therein is particularly appropriate to inorganic determinations. The type of volumetric glassware to be used, the effect of certain reagents on glassware, the effect of temperature on volumetric measurements, purity of reagents, absorption of gases and water vapor from the air, standardization of solutions, instability, and need for frequent standardization of certain reagents are among the topics discussed. It is recommended that the analyst become thoroughly familiar with these publications.

5.2.1 General Inorganic Analyses

In general, AR-grade reagents and solvents are satisfactory for inorganic analyses. Primary standard reagents must, of course, be used for standardizing all volumetric solutions. Commercially prepared reagents and standard solutions are very convenient and may be used when it is demonstrated that they meet the method requirements. All prepared reagents must be checked for accuracy.

The individual methods specify the reagents that require frequent standardization, or other special treatment, and the analyst must follow through with these essential operations. To avoid waste, the analyst should prepare a limited volume of such reagents, depending on the quantity required over a given period of time. Examples and brief discussions of the kind of problems that occur are given under Paragraph 5.3, "Elimination of Determinate Errors".

As far as possible, distilled water used for preparation of reagent solutions must be free of measurable amounts of the constituent to be determined. Special requirements for distilled water are given in Chapter 3 of this manual and in individual method descriptions.

Compressed gases, such as oxygen and nitrogen, used for total organic carbon determination may be of commercial grade.

5.2.2 Metals Analyses

All standards used for atomic absorption and emission spectroscopy should be of spectroquality. It is recommended that other reagents and solvents also be of spectroquality, although AR grade is sometimes satisfactory. Standards may be prepared by the analyst in the laboratory or prepared, spectrographically standardized materials may be purchased commercially. Standards required for determination of metals in water are not generally available from the National Bureau of Standards.

Analytical reagent grade nitric and hydrochloric acids must be specially prepared by distillation in borosilicate glass and diluted with deionized distilled water. All other reagents and standards are also prepared in deionized water.

In general, fuel and oxidant gases used for atomic absorption can be of commercial grade. Air supplied by an ordinary laboratory compressor is quite satisfactory, if adequate pressure is maintained and necessary precautions are taken to filter oil, water, and possible trace metals from the line. For certain determinations, e.g., aluminum, reagent-grade nitrous oxide is required.

5.2.3 Radiological Analyses

The great sensitivity of radioactive counting instruments requires that scintillation grade reagents and solvents, or equivalent, be used for all radioactivity determinations. Some of the reagents, for example, strontium carbonate and yttrium oxide carriers used for the determination of strontium 90 and yttrium 90, must be stable, that is free of radioactivity. Barium sulfate, used for coprecipitation of radium must be free from all traces of radium. These reagents and solvents are commercially available from chemical supply houses.

Calibrated standard sources of specific radioactive materials with known count and date of counting are available from various suppliers. No single company supplies all standards.

Gases used for radioactive counting must be of high purity and extra dry. Gases such as helium and air are aged for about 30 days to allow radioactive background to decay. All gases are checked for background before use. Some cylinders contain inherent radioactivity which is imparted to the gas. When this background is above normal, the gas should not be used for radioactivity determinations.

5.2.4 Organic Chemical Analyses

The minimum purity of reagents and solvents that can be used for organic analyses is AR grade. Reference grade standards should be used whenever available. Special note should be taken of the assay of standard materials. Owing to the great sensitivity (nanogram and subnanogram quantities) of gas chromatography (GC), which is often used to quantitate organic results, much greater purity is frequently required (6). The specificity of some GC detectors requires that reagents and solvents be free of certain classes of compounds. For example, analyses by electron capture require that reagents and solvents be free of electronegative materials that would interfere with the determination of specific compounds in the sample. Similarly, use of the flame photometric detector requires that reagents and solvents be free from sulfur and/or phosphorus interference. Pesticide quality solvents are available from several sources. These are often satisfactory for many organic GC determinations. However, the contents of each container must be checked to assure its suitability for the analyses. Similarly, all analytical reagents and other chemicals must also be checked routinely.

The quality of gases required for GC determinations varies somewhat with the type of detector. In general, the compressed gases are a prepurified dry grade. Grade A helium from the U.S. Bureau of Mines has always been satisfactory. The Dohrmann nitrogen-detection system requires the use of ultra-pure hydrogen for satisfactory results. The use of molecular-sieve, carrier-gas filters and drying tubes is required on combustion gases. They are recommended for use on all other gases. It is recommended that the analyst familiarize himself with an article by Burke (7) on practical aspects of gas chromatography.

All reagents, solvents, and adsorbents used for thin-layer chromatography must be checked to be certain that there are no impurities present that will react with the chromogenic reagent or otherwise interfere with subsequent qualitative or quantitative determinations. Glass-backed layers prepared in the laboratory or precoated layers supplied by a manufacturer may be used. However, precoated layers are more difficult to scrape.

Therefore, it is recommended that layers prepared in the laboratory be used when zones are to be scraped in order to recover isolated compounds. Plastic-backed layers are generally unsatisfactory for this type of analysis.

Adsorbents most commonly used for column chromatographic clean-up of sample extracts are Florisil, silica gel, and alumina. These must be pre-activated according to the method specifications and checked for interfering constituents.

5.3 Elimination of Determinate Errors

In order to produce high quality analytical data, determinate errors must be eliminated or at least minimized. For purposes of this discussion, we assume that a competent analyst and reliable equipment, in optimum operating condition, are available. Thus, determinate errors that might result from an inexperienced or careless analyst and poor equipment are eliminated. The remaining sources of error are the reagents, solvents, and gases that are used throughout the analyses. The quality of these materials, even though they are AR grade or better, may vary from one source to another, from one lot to another, and even within the same lot. Therefore, the analyst must predetermine that all of these materials are free of interfering substances under the conditions of the analyses. To do this he must have a regular check program. Materials that do not meet requirements are replaced or purified so that they can be used.

5.3.1 Reagent Blank

The first step the analyst must take is to determine the background or blank of each of the reagents and solvents used in a given method of analysis. The conditions for determining the blank must be identical to those used throughout the analysis, including the detection system. If the reagents and solvents contain substances that interfere with a particular determination, satisfactory reagents and solvents must be found. Where possible and practical, they should be treated so that they can be used.

5.3.2 Method Blank

After determining the individual reagent or solvent blanks, the analyst must determine the method blank to see if the cumulative blank interferes with the analyses. The method blank is determined by following the procedure step by step, including all of the reagents and solvents, in the quantity required by the method. If the cumulative blank interferes with the determination, steps must be taken to eliminate or reduce the interference to a level that will permit this combination of solvents and reagents to be used. If the blank cannot be eliminated, the magnitude of the interference must be considered when calculating the concentration of specific constitutents in the samples being analyzed.

A method blank should be determined whenever an analysis is made. The number of blanks to be run is determined by the method of analysis and the number of samples being analyzed at a given time. In some methods, such as the AutoAnalyzer procedures, the method blank is automatically and continuously compensated for since a continuous flow of the reagents passes through the detector. In other procedures, such as the gas chromatographic determination of pesticides, a method blank is run with each series of samples analyzed. Usually this is one blank for every nine samples.

5.3.3 Elimination of Interferences and Other Sources of Error

Procedures for eliminating or at least minimizing impurities that produce specific interferences or high general background, vary with the reagent and method involved. These procedures may include: recrystallization, precipitation, distillation, washing with an appropriate solvent, or a combination of these. Examples of procedures used for various types of analyses are given below. For complete information, the analyst should consult the individual methods.

5.3.3.1 General Inorganic Analyses

Analytical reagent grade chemicals and solvents usually present no interference problems in inorganic analyses. However, some reagents do not always meet methods requirements. An example is potassium persulfate used in phosphorus and nitrogen determinations. This reagent is frequently contaminated with ammonia. Therefore, it is routinely purified by passing air through a heated water solution of the reagent. The purified potassium persulfate is recovered by recrystallization.

A problem more commonly encountered in inorganic analyses is the rapid deterioration of the standard reagents and other ingredients. To minimize or eliminate this problem some reagents, for example, ferrous ammonium sulfate, must be standardized daily. Others, such as sodium thiosulfate used for dissolved oxygen determination, may require a substitute reagent, e.g., phenyl arsene oxide. Solid phenol which readily oxidizes and acquires a reddish color can be purified by distillation. Starch indicator used for idiometric titrations may be prepared for each use or preserved by refrigeration, or by addition of zinc chloride or other suitable compounds.

5.3.3.2 Metals Analyses

In general, spectrograde chemicals, solvents, and gases present no interference problems in atomic absorption or emission spectrographic determinations. However, standards which do not meet the requirements of the method are sometimes obtained. Ordinarily, no effort is made to purify them. They are simply replaced by new reagents of sufficient purity. Some reagents may form precipitates on standing. Such reagents will reduce the accuracy of quantitative analyses and should not be used.

5.3.3.3 Radiological Analyses

In general, reagents that do not meet the purity requirements for radiological determinations are replaced with reagents that are satisfactory. However, in some instances (for example, barium sulfate used for coprecipitation of radium), it may be necessary to carry out repeated recrystallization to remove all forms of radium, and reduce the background count to a useable level. In some instances, solvents that do not meet requirements may be distilled to produce adequate purity. In some cases, gases having background counts may be useable after aging as described earlier. If not, they should be replaced with gases that are satisfactory.

5.3.3.4 Organic Analyses

Many AR-grade chemicals and solvents, and at times pesticide quality solvents, do not meet the specifications required for the determination of specific organic compounds. Impurities that are considered trace, or insignificant, for many analytical uses, are often present in greater quantities than the organic constituents being measured. Coupled with the several-hundred-fold concentration of the sample extract that is usually required, such impurities can cause very significant interferences in trace organic analyses. Reagents and solvents found to be unsatisfactory, under the conditions of the analyses, must be replaced or cleaned up so that they are useable. Some useful clean-up procedures are:

a. Washing the inorganic reagents with each solvent that the reagent contacts during the analysis,

b. Washing the adsorbents, such as silica gel G and Florisil, with the solvents that are used for a specified column or thin-layer chromatographic procedure,

c. Pre-extracting distilled water with solvents used for the particular analysis involved,

d. Pre-extracting aqueous reagent solutions with the solvents involved,

e. Redistilling solvents in all-glass systems using an efficient fractionating column,

f. Recrystallizing reagents and dyes used in colorimetric or thin-layer determinations,

If the reagents and solvents thus produced are not of sufficient purity, they should be replaced.

Dirty gases (quality less than specified) are particularly troublesome in gas chromatographic analyses. They may reduce the sensitivity of the detector, and produce a high or noisy baseline. If this occurs, the cylinder should be replaced immediately. Similarly, if cylinders of compressed gases are completely emptied in use, the end volumes of the gas may produce a similar and often more severe effect. Oils and water may get into the system and foul the detector. When this occurs the system must be dismantled and cleaned. Overhaul of the detector may be required. To reduce chances of this, it is recommended that all gas cylinders be replaced when the pressure falls to 100-200 psi. Filter driers are of little help in coping with this type of contamination.

5.3.4 Storing and Maintaining Quality of Reagents and Solvents

Having carried out the tasks of selecting, preparing, and verifying the suitability of reagents, solvents, and gases, the analyst must properly store them to prevent contamination and deterioration prior to their use. Borosilicate glass bottles with ground glass stoppers are recommended for most standard solutions and solvents. Plastic containers, e.g., polyethylene, are recommended for alkaline solutions. Plastic containers must not be used for reagents or solvents intended for organic analyses. However, plastic containers may be used for reagents not involved with organic analyses if they maintain a constant volume, and it is demonstrated that they do not produce interferences and do not absorb constitutents of interest. It is important that all containers be properly cleaned and stored prior to use. (Refer to Chapter 4 for details).

Standard reagents and solvents must always be stored according to the manufacturer's directions. Reagents or solvents that are sensitive to the light should be stored in dark bottles and/or stored in a cool, dark place. It is particularly important to store materials used for radiological determinations in dark bottles, since photoluminescence will produce high background if light sensitive detectors are used for counting. Some reagents require refrigeration.

Adsorbents for thin-layer and column chromatography are stored in the containers that they are supplied in, or according to the requirements of individual methods. Activated carbon, used for collection of samples for organic analyses, must be stored and processed in areas protected from atmospheric and other sources of contamination (8).

The analyst should pay particular attention to the stability of the standard reagents. Standards should not be kept longer than recommended by the manufacturer, or in the method. Some standards are susceptible to changes in normality due to absorption of gases or water vapor from the air. Provisions for minimizing this effect are given in Part 23 of ASTM Standards (4).

The concentration of the standards will change as a result of evaporation of solvent. This is especially true of standards prepared in volatile organic solvents. Therefore, the reagent bottles should be kept stoppered, except when actually in use. The chemical composition of certain standards may change on standing. Certain pesticides, for instance, will degrade if prepared in acetone that contains small quantities of water. Thus, it is essential that working standards be frequently checked to determine changes in concentration or composition. Stock solutions should be checked before preparing new working standards from them.

5.4 References

1. National Bureau of Standards, Special Publication 260, "Standard Reference Materials", July 1969.

2. "Reagent Chemicals, American Chemical Society Specifications", American Chemical Society, Washington, D.C.

3. ASTM Special Technical Publication No. 148-H, "Manual on Industrial Water and Industrial Waste Water", 2nd Edition, p. 869 (1965).

4. 1968 Book of ASTM Standards, Part 23; p. 897: American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103.

5. Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Association, New York (1971).

6. "FWPCA Method for Chlorinated Hydrocarbon Pesticides in Water and Waste Water", Federal Water Pollution Control Administration, Analytical Quality Control Laboratory, November 1969.

7. Burke, J., JAOAC, 48, 1037 (1965).

8. Breidenbach, A. W., et al, "The Identification and Measurement of Chlorinated Hydrocarbon Pesticides in Surface Waters", Publication WP-22, Federal Water Pollution Control Administration, Washington, D.C. (November 1966).

Chapter 6

CONTROL OF ANALYTICAL PERFORMANCE

6.1 Introduction

This chapter is limited to a discussion of the control of analytical performance in the laboratory. It is assumed that a valid sample has been properly taken, preserved, and delivered to the laboratory for analyses; that the laboratory analyses were done according to currently-recognized methods; and that the recording and reporting of subsequent laboratory results were done in a systematic, uniform, and permanent fashion (See Chapter 7). It must be recognized (and practiced!), however, that quality control begins with the sample collection and does not end until the resulting data are reported. The laboratory control of analytical performance is but one vital link in obtaining valid data. A continuous rapport and conscientious use of quality control between field sampling, laboratory analyses, and management decisions are necessary to insure this validity.

Earlier chapters have discussed such key elements as laboratory services, instrumentation, glassware, reagents, solvents, and gases; the reader should refer to these sections to determine the necessary specifications and requirements required for quality control. On the assumption that these variables are under control, that a single method is being used, and that the complete system is initially under control, what should be done in the evaluation of daily performance to document that valid data are being produced? First, valid precision and accuracy data should be available on the method and analyst. Thereafter, systematic daily checks are required to show that reproducible results are being obtained, and that the methodology is actually measuring what is in the sample. These items are discussed in detail in the following sections.

6.2 Precision and Accuracy

Precision refers to the reproducibility among replicate observations. In an Analytical Quality Control Program, it is determined, not on reference standards, but by the use of actual water samples which cover a range of concentrations and a variety of interfering materials usually encountered by the analyst. Obviously, such data should not be collected until the analyst is thoroughly familiar with the method, and has obtained a reproducible standard curve. For colorimetric analyses, the initial standard curve should include a blank and a series of at least eight standards encompassing the full concentration range to be used for routine sample analyses. Subsequently, at least two standards (a high and a low) should be analyzed to verify the original standard curve. For other measurements, such as pH, conductivity, turbidity, etc., instruments should be standardized according to manufacturer's instructions (See Chapter 3) and sound, scientific practice.

There are a number of different methods available for the determination of precision. One method that has been successfully employed by experienced AutoAnalyzer users, and can be adapted to many other analytical instrumentation and chemical procedures, is described as follows:

a. Four separate concentration levels should be studied, including a low concentration near the sensitivity level of the method, two intermediate concentrations, and a concentration near the upper limit of application of the method.

b. Seven replicate determinations should be made at each of the concentrations tested.

c. To allow for changes in instrument conditions, the precision study should cover at least two hours of normal laboratory operation.

d. In order to permit the maximum interferences in sequential operation, it is suggested that the samples be run in the following order: high, low, intermediate, intermediate. This series is then repeated seven times to obtain the desired replication.

e. The precision statement should include a range of standard deviations over the tested range of concentration. Thus, four standard deviations will be obtained over a range of four concentrations, but the statement should contain only the extremes of standard deviations and concentrations studied.

An example of data generated from such an approach is shown in Table 6-1.

Table 6-1

PRECISION DATA ON RIVER WATER SAMPLES FOR PHOSPHORUS AUTOANALYZER METHOD

	Conc., (mg P/1)			
Sample	Kanawha	Klamath	Arkansas	Big Souix
1	0.05	0.10	0.48	0.62
2	0.06	0.10	0.48	0.62
3	0.06	0.10	0.49	0.62
4	0.06	0.11	0.48	0.63
5	0.06	0.11	0.48	0.62
6	0.06	0.11	0.48	0.62
7	0.06	-	-	0.62
Avg.	0.059	0.105	0.482	0.621
s	0.004	0.005	0.004	0.004

The resulting precision statement would read as follows:

> "In a single laboratory, using surface water samples at concentrations of 0.06 and 0.62 mg P/1, the standard deviation was ±0.004 (Analytical Quality Control Laboratory)."

Thus, the statement contains the number of laboratories involved, the type of samples, the concentrations used, the resulting standard deviation (s) and the reference source.

Accuracy refers to a degree of difference between observed and known, or actual, values. Again, accuracy should be determined on actual water samples routinely analyzed, and preferably, on the same series as those used in the precision determinations. The method employed by experienced AutoAnalyzer users consists of the following key steps:

a. Known amounts of the particular constituent should be added to actual samples at concentrations where the precision of the method is satisfactory. It is suggested that amounts be added to the low-concentration sample, sufficient to double that concentration, and that an amount be added to one of the intermediate concentrations, sufficient to bring the final concentration in the sample to approximately 75% of the upper limit of application of the method.

b. Seven replicate determinations at each concentration should be made.

c. Accuracy should be reported as the percent recovery at the final concentration of the spiked sample. Percent recovery at each concentration should be the mean of the seven replicate results.

Data were obtained with this approach by using two of the water samples previously used in the precision study reported in Table 6-1 (Kanawha and Arkansas Rivers). They are reported in Table 6-2.

Table 6-2

ACCURACY DATA ON RIVER WATER SAMPLES FOR PHOSPHORUS AUTOANALYZER METHOD

	Conc., (mg P/1)	
Sample	Kanawha (Added 0.06 mg/1P)	Arkansas (Added 0.3 mg/1 P)
1	0.105	0.74
2	0.105	0.75
3	0.105	0.75
4	0.110	0.73
5	0.110	0.74
6	0.110	0.75
7	0.105	0.75
Avg.	0.107	0.74
% Recovery	$\left[\frac{0.107}{0.059 + 0.06}\right] \times 100 = 90$	$\left[\frac{0.74}{0.48 + 0.30}\right] \times 100 = 95$

Again, in order to contain the key elements, the accuracy statement would read as follows:

> "In a single laboratory, using surface water samples at concentrations of 0.11 and 0.74 mg P/1, recoveries were 90% and 95%, respectively (Analytical Quality Control Laboratory)".

Once collected and documented, these precision and accuracy data may be used in a number of ways. Two important examples are: (1) They present clearcut evidence that the analyst in question is indeed capable of analyzing the water samples for that particular parameter. That is, he has the standard method under control, and is capable of generating valid data; and (2) the data can be used in the evaluation of daily performance in reference to replicate samples, spiked standards and samples, and in the preparation of quality control charts.

As observed, the above methods can be adapted to other chemical procedures and analytical instruments. They have been used on manual titration methods for such parameters as alkalinity, chloride, and hardness; on general inorganic instruments such as pH, conductivity, selective ion, and turbidity meters; and on the Beckman Carbonaceous Analyzer. Other instruments, such as atomic absorption and flame emission spectrophotometers, could also be evaluated by these methods; however, radiological instrumentation and gas chromatography systems (See Chapter 8) require special techniques.

6.3 Evaluation of Daily Performance

Once valid precision and accuracy data are available on the method and the analyst, systematic daily checks are necessary to insure that valid data are being generated. First of all, verification of the originally-constructed standard curve is mandatory. As previously noted, at least two standards (a high and a low) should be analyzed routinely along with a blank to determine that comparable operating conditions exist. If the data do not substantiate such control, the analyst must systematically trouble-shoot his system until the problem is corrected.

In order to document that reproducible results are being obtained (i.e., precision of the method), it is necessary to run replicate samples. Although frequency of such replicate analyses is, by nature, dependent on such factors as the original precision of the method, the reliability of the instrumentation involved, and the experience of the analyst, good laboratory technique is to run duplicate analyses at least ten percent of the time. The resulting data should agree favorably with the known precision of the method. If they do not, the system is not under control, and results are subject to question.

Concurrently, quality control should include assurance that the daily system is actually measuring what is in the sample (i.e., accuracy of the method). Although it is far preferable to have obtained values check with known or actual values, it should be recognized that inaccuracy does not destroy the value of data if the degree and precision of the error is known and taken into account. In order to account for background contamination and/or sample interferences, and as a matter of routine practice, spiked samples should be used in addition to standards. As in the case of duplicate sample analyses, good laboratory technique dictates that spiked samples be run at least ten percent of the time.

Thus, daily control of analytical performance in the laboratory requires approximately 15-20 percent of the analyst's time. Considering the elapsed time and combined efforts of skilled personnel that are represented in a final laboratory result, this is a comparatively small price to pay for, not a "number", but a valid concentration value.

A most convenient way of recording the obtained precision and accuracy data is through the preparation of quality control charts. Plotting of said data systematically answers the question as to whether the laboratory analyses are under control, and is useful in observing developing trends of positive or negative bias. Because of its importance in documenting the quality control being practiced daily in the laboratory, the construction and uses of quality control charts are treated as a separate topic in the next section.

A broader and somewhat different form of evaluation of daily performance may be made through routine participation in interlaboratory round-robin studies. Samples analyzed in such a cooperative program should be treated as part of the routine sample load. In so doing, the analyst is able to compare his individual performance against other laboratory personnel, and to have a reliable measure of the particular method's capabilities. In many respects such samples can be regarded as reputable "blind samples"; a necessary ingredient in the quality control of laboratory results.

6.4 Quality Control Charts

Quality control charts were originally developed for the control of production processes where large numbers of items were being manufactured and inspected on an essentially continuous basis. As shown in Figure 6-1, a control chart consists of a graphical chart with the vertical scale plotted in units of the test result and the horizontal scale in units of time or sequence of results. The upper and lower control limits shown on the chart are used as criteria for action, or for judging the significance of variations between duplicate samples. The central line represents the average or the standard value of the statistical measure being plotted.

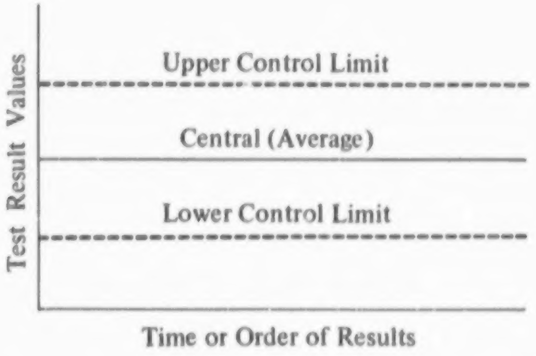


Figure 6-1 ESSENTIALS OF CONTROL CHART

As observed in the previous section on the evaluation of daily performance, daily precision and accuracy data can be plotted by means of these quality control charts to determine if valid, questionable, or invalid data are being generated from day to day. There are several techniques available for actually constructing quality control charts and plotting subsequent data. Two currently in use are the Shewhart technique (1,2) and the CuSum technique (3). In both techniques, precision control charts are constructed from duplicate sample analyses, whereas, accuracy control charts are constructed from spiked samples or standards data generated in monitoring recovery efficiencies. At least 15 to 20 sets of duplicate and 15 to 20 sets of spiked sample data from an in-control process are necessary for the initial construction. A system is initially said to be in control when the standard deviation and recovery efficiency data for a given parameter are comparable to those obtained by other experienced laboratories. It is also necessary that the initial and subsequent sets of data be obtained under normal laboratory operation conditions, that the same analyst or group of analysts run the analysis, and that the same analytical method is used.

6.4.1 Cumulative-Summation (CuSum) Quality Control Charts

There are various systems currently available for plotting data in the form of cumulative sum charts (4). One system that has been in continuous use within EPA Region VI is that of Harkins and Crowe (3). It has proved most useful in monitoring the validity of data generated by a contracting laboratory and is currently being used routinely to daily record intra-laboratory performance in technical operations. The following material has been excerpted from their manual (3), in order to accurately describe the construction and use of these charts:

6.4.1.1 Construction of CuSum Quality Control Charts

The control charts are derived from three basic calculations:

a. Standard deviations (S_d) of the differences between duplicates or, in the case of spiked or standard samples, between the known quantity and the quantity obtained.

b. The upper control limit (UL)

c. The lower control limit (LL)

Prior to these calculations, two decisions must be made:

a. The α and β levels

b. The allowable variability levels

Mathematical Equations

$$S_d^2 = \frac{\sum_{i=1}^{n} di^2 - \frac{(\sum_{1}^{n} di)^2}{N}}{N-1} = \text{Variance of the differences}$$

$$S_d = \sqrt{S_d^2} = \text{Standard deviation of the differences} \qquad \text{(a)}$$

$$S_0^2 = (.8S_d)^2 = .64\ S_d^2 \text{ (estimates } \sigma_0^2\text{)}$$

$$S_1^2 = (1.2S_d)^2 = 1.44\ S_d^2 \text{ (estimates } \sigma_1^2\text{)}$$

$$UL(M) = \frac{2 \log_e \left[\frac{1-\beta}{\alpha} \right]}{\frac{1}{S_0^2} - \frac{1}{S_1^2}} + M \frac{\log_e \left[\frac{S_1^2}{S_o^2} \right]}{\frac{1}{S_0^2} - \frac{1}{S_1^2}}$$

$$LL(M) = \frac{2 \log_e \left[\frac{\beta}{1-\alpha} \right]}{\frac{1}{S_0^2} - \frac{1}{S_1^2}} + M \frac{\log_e \left[\frac{S_1^2}{S_0^2} \right]}{\frac{1}{S_0^2} - \frac{1}{S_1^2}}$$

Where: UL(M) = upper limit at M sets of samples

LL(M) = lower limit at M sets of samples

di = the difference between the i^{th} set of duplicates or spiked samples

N = the total number of sets of duplicates or spiked samples used to construct the control charts

S_0^2 = minimum amount of variation allowed in the system

S_1^2 = maximum amount of variation allowed in the system

α = percent (decimal fraction) of time you are willing to judge the procedure out of control when it is in control

β = percent (decimal fraction) of time you are willing to judge the procedure in control when it is out of control

M = number of sets of duplicates or spiked samples used in calculating the value to be plotted on the chart

By definition, α is the probability of judging the process to be out of control when in fact, it is in control. It is recommended that α be chosen to lie between the boundaries of .05 and .15, that is, the laboratory personnel are willing to stop the laboratory process somewhere between 5 and 15% of the time, judging it to be out of control, when in fact, it is in control. If the cost of examining a process to determine the reason or reasons for being out of control is considerable, then it may be desirable to choose a low α. Likewise, if the cost is negligible, it may be desirable to choose a larger α value, and thus stop the process more frequently. (See Figure 6-2)

On the other hand, β is defined as the probability of judging the process to be in control when it is not. Again, it is recommended that β be chosen to lie between the values of .05 and .15; thus, the laboratory personnel are willing to accept out of control data somewhere between 5 and 15% of the time. The economic considerations used for choosing α are also applicable to the choice of B. (See Figure 6-2.)

It is also essential to set maximum and minimum allowable variability levels. It is necessary to specify a value for the minimum and maximum amount of variation that will be allowable in the system. These minimum and maximum amounts are referred to as σ_0^2 and σ_1^2 respectively. The values used should be based on a knowledge of the variation in the procedure under consideration. However, if such knowledge is not available, the values may be arbitrarily set at $\sigma_0^2 = (\sigma - .20\sigma)^2$ and $\sigma_1^2 = (\sigma + .20\sigma)^2$.

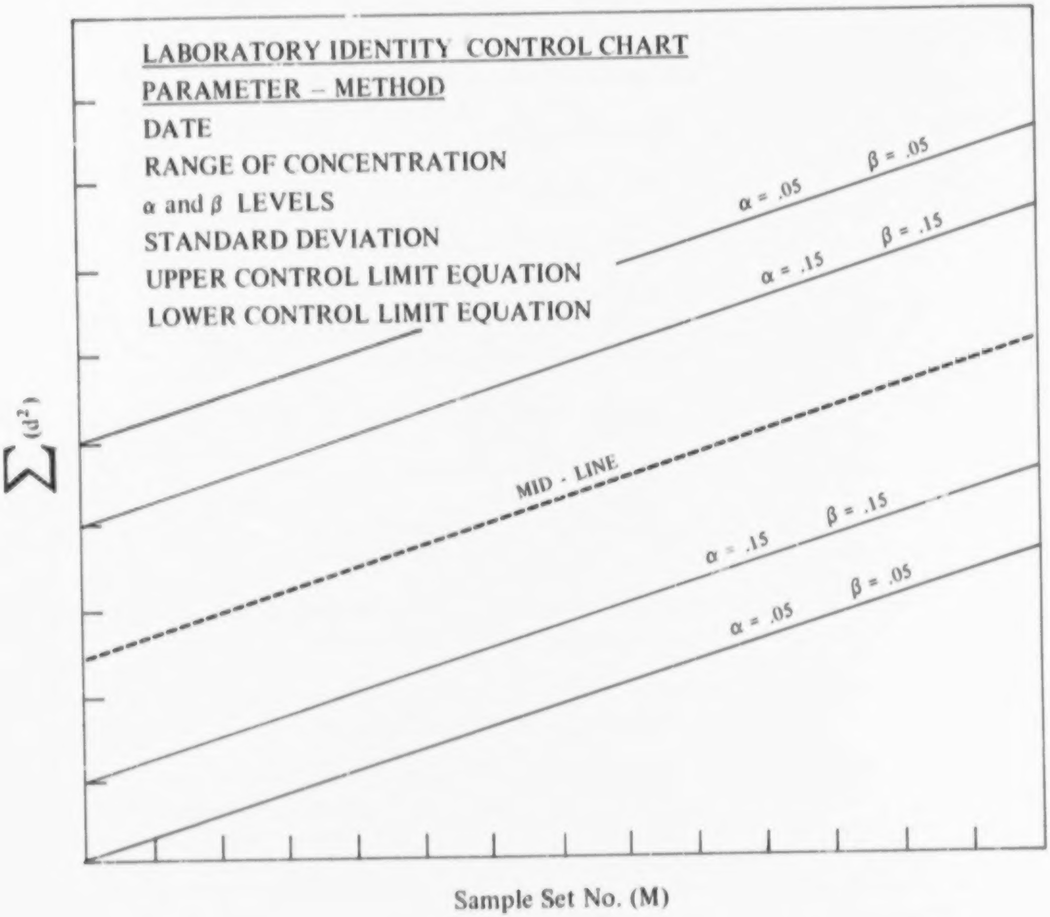


Figure 6-2. EFFECT OF α AND β LEVELS ON STANDARD CONTROL CHART

6.4.1.2 Use of CuSum Control Charts

Once the control charts are constructed, and prior to their use, consideration must be given to the number of duplicate analyses to be conducted during a series of samples; likewise, the same decision must be made on spiked or standard samples.

In considering the number of duplicate and spiked sample analyses to be conducted in a series of samples, it is necessary to weight the consequences when the data go out of control. The consequences of this situation are reanalyzing a series of samples or discarding the questionable data obtained. The samples to be reanalyzed are those lying between the last in-control point and the present out-of-control point. A realistic frequency for running duplicate and spiked samples would be every fifth sample; however, economic consideration and experience may require more or less frequent duplicate and spiked sample analyses.

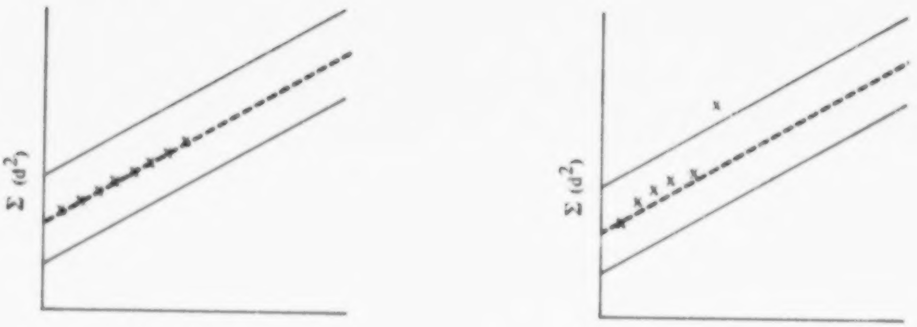
Once the frequency of duplicate and spiked samples has been determined, it is then necessary to prepare spiked or standard samples in concentrations relative to the concentration of the control charts, which should be similar to those of the environmental samples. These spiked or standard samples must be intermittently dispersed among the series of samples to be analyzed and without the analyst's knowledge of concentration. Similarly, duplicate samples must be intermittently dispersed throughout the series of samples to be analyzed, and ideally, without the analyst's knowledge; however, this is sometimes very difficult to accomplish.

The results of the duplicate and spiked sample analyses should be calculated immediately upon analyzing the samples to allow for early detection of problems that may exist in the laboratory. An example of these calculations follows:

Duplicate Sample No. M	Results No. 1	No. 2	Difference (di)	di^2	$\Sigma(di^2)$
1	5.4	5.2	.2	.04	.04
2	4.8	4.7	.1	.01	.05
3	6.1	5.8	.3	.09	.14

Upon plotting the summation or $\Sigma(di^2)$, one of three possibilities can occur (See Figure 6-3):

a. Out of control on the upper limit
When data goes out of control on the upper limit the following steps should be taken:
    1. Stop work immediately
    2. Determine problems
        (a) Precision control chart
            (1) The analyst
            (2) Nature of the sample
            (3) Glassware contamination

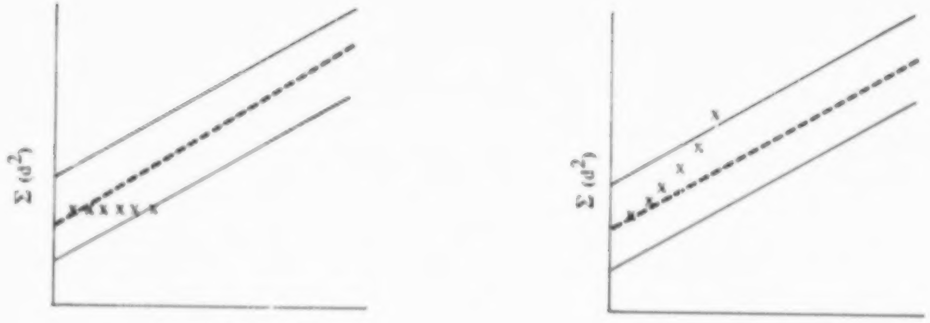


ANALYSIS IN CONTROL

NO PROBLEMS:
CONTINUE ANALYSIS

ANALYSIS OUT OF CONTROL
UPPER LIMIT

PROCEDURES:
1. STOP ANALYSIS
2. LOCATE PROBLEM
3. CORRECT PROBLEM
4. RERUN SAMPLES
5. START CHART AT SAMPLE SET NO. 1.



ANALYSIS OUT OF CONTROL
LOWER LIMIT

INCREASED EFFICIENCY OR FALSE REPORTING
PROCEDURES:
1. CONTINUE ANALYSIS
2. CONSTRUCT NEW CHART WITH RECENT DATA
3. OBSERVE ANALYST

ANALYSIS OUT OF CONTROL
UPPER LIMIT

CONTINUOUS ERROR TREND
PROCEDURES:
SAME AS ABOVE BUT STOP ANALYSIS WHEN TREND IS DETECTED.

Figure 6-3. LABORATORY QUALITY CONTROL CHARTS

    (b) Accuracy control chart
        (1) The analyst
        (2) Glassware contamination
        (3) Contaminated reagents
        (4) Instrument problems
        (5) Sample interference with the spiked material
3. Rerun samples represented by that sample set number, including additional duplicate and spiked samples.
4. Begin plotting at sample No. 1 on chart.

b. In control within the upper and lower limit lines

When data continuously fall in between the upper and lower control limits, the analyses should be continued until an out-of-control trend is detected.

c. Out of control on the lower limit

When data fall out of control on the lower limit, the following steps should be taken:

1. Continue analyses unless trend changes
2. Construct new control charts on recent data
3. Check analyst's reporting of data

6.4.2 Shewhart Quality Control Charts

Dr. Walter A. Shewhart of Bell Telephone Laboratories developed the basic theory of control charts in the 1920's. His book on statistical quality control (1) grew out of this original work. Since then, industrial acceptance of these control chart concepts and other statistical techniques have refined and quantitated the quest for quality in manufacturing. Although originally developed for control of production processes when large numbers of articles were being manufactured and inspected on an essentially continuous basis, these same concepts have been readily adapted to laboratory operations where the analyst produces comparatively fewer results on an intermittent basis.

As in the CuSum approach, precision control charts are prepared from data resulting from duplicate sample analyses and accuracy control charts from duplicate spiked standards or samples. Once the control charts are constructed, however, data are plotted as individual values rather than cumulative sums.

Certain constants (factors) are also involved in the preparation of Shewhart Charts. Depending upon how the data are grouped, what the size of each grouping is, and what control limit formulation is being calculated, Table 6-3 will serve as a basic reference point:

Table 6-3

FACTORS FOR COMPUTING CONTROL CHART LINES (5, 6)

Observations in Subgroup (n)	Factor A_2	Factor D_4
2	1.88	3.27
3	1.02	2.58
4	0.73	2.28
5	0.58	2.12
6	0.48	2.00
7	0.42	1.92
8	0.37	1.86

Inherent in the Shewhart approach is recognition of the basic assumption that variations exist in every method. That is, no procedure is so perfect, so unaffected by its environment, that it will always give exactly the same assay value or product. Where such situations seem to exist, either the device used to measure the process is not sensitive enough or the person making the measurements is not performing properly. For our purposes, the recorded difference between paired samples should never be less than one-half the minimum detectable limit of the parameter under consideration. In the following outlines for preparing precision and accuracy control charts, nitrate data were used to develop the examples. Therefore the minimum values shown are 0.05 (one-half the observed minimum detectable limit of 0.1 mg/l as N).

6.4.3 Precision Control Charts

These charts are developed by collecting data for many samples, a minimum of 15 to 20, run in duplicate under assumed controlled conditions. Once these data have been generated, preferably over an extended period of laboratory time, the following steps should be followed to construct the control chart:

a. List the range (R) for each set of samples. That is, the absolute value of the difference between each set of duplicate samples.

Note: The following ranges were observed in the nitrate data:

0.1
0.05
0.05
0.05
0.05
0.05
0.05
0.05
0.05
0.05
0.05
0.05

0.1
0.05
0.05
0.05
0.30
0.10
0.05
0.05
0.05
0.05
0.05
0.05

0.05
0.05
0.05
0.05
0.05
0.05
0.05
0.05
0.05
0.05
0.05

b. Calculate the average range ($\bar{R}$) by summing the list of R values and dividing by the number of sets of duplicates:

$$\bar{R} = \frac{\Sigma R}{\eta}$$

$$\bar{R} = \frac{2.15}{35} = 0.06$$

c. Calculate the Upper Control Limit (UCL) on the range according to the formula:

$$UCL_R = D_4 \bar{R},$$

where D_4 is a constant dependent on the number of units in the subgroup. In this case, since two observations are in the subgroup, $d_4 = 3.27$ (see Table 6-3).

$$UCL_R = 3.27\ \bar{R} = 0.20$$

d. Calculate the Upper Warning Limit (UWL) on the range according to the formula:

$$UWL_R = 2/3\ (D_4 \bar{R} - \bar{R}) + \bar{R},$$

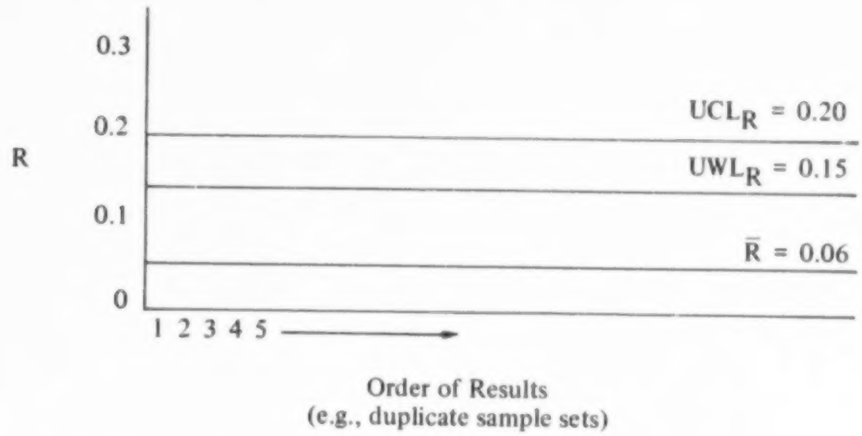
which for duplicate samples reduces to

$$UWL_R = 2.51\ \bar{R}$$

$$UWL_R = 0.15$$

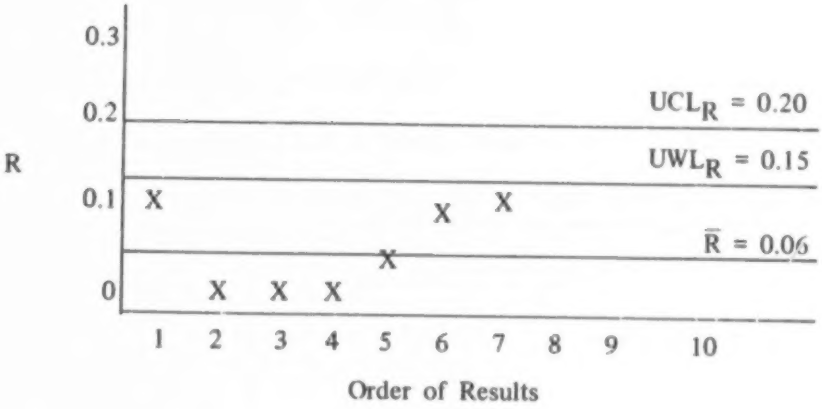
This UWL corresponds to the 95% confidence level.

e. Now graph $\bar{R}$, UWL_R, and UCL_R in the following manner:

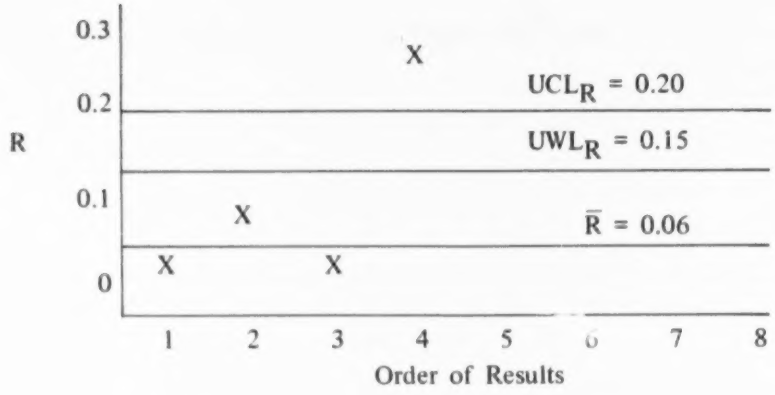


f. The above precision control chart for nitrates is now complete, and can be used to plot R values on subsequent duplicate samples to determine if the system is in control, out of control (plotted R value beyond the UCL), and/or to detect any trends developing within the system.

1. In this example, a trend has developed between duplicate sample sets 4 thru 7. Although the system is not out of control, all variables in the procedure should be checked in an attempt to stop this obvious trend before the UCL is reached.



2. In this example, the system has clearly gone out of control between duplicate samples 3 and 4. At this point, the system can be stopped and all variables in the system checked, or another set of duplicate samples can be run to verify the observed difference. Once the system has been corrected, all samples between set 3 and 4 should be rerun to insure the validity of the data.



6.4.4 Accuracy Control Charts

As in the above system, these charts are developed by collecting data for many samples, a minimum of 15 to 20, but on spiked samples (preferably) or standards under assumed controlled conditions. Again, these data should be generated over an extended period of laboratory time, and be representative of normal operating conditions (7). The following steps should be followed to construct accuracy control charts:

a. List the range (R) and the average ($\bar{X}$)* of each subgroup of data.
Note: In the following example of nitrate data, subgroups of monthly data involving four observations were used:

$$*\bar{X} = \frac{\Sigma d \text{ Found - Actual}}{n}$$

Month	Actual	Found	R	$\bar{X}$
Sept.	1.1	1.1		
	1.1	1.1	0	0
	1.1	1.1		
	1.1	1.1		
Nov.	1.1	1.1		
	1.1	1.1	0.1	-0.025
	1.2	1.2		
	1.2	1.1		
Dec.	1.0	1.1		
	1.0	1.0	0.1	+0.025
	1.0	1.0		
	1.0	1.0		
Jan.	1.0	0.9		
	1.0	1.0	0.2	0
	1.0	1.1		
	1.0	1.0		

b. Calculate the average range ($\overline{R}$) by summing the list of R values and dividing by the number of subgroups:

$$\overline{R} = \frac{\Sigma R}{\eta}$$

$$\overline{R} = \frac{0.4}{4} = 0.10$$

c. Calculate the Upper Control Limit (UCL) on the range according to the formula:

$$UCL_R = D_4\overline{R},$$

where D_4 is a constant dependent on the number of units in the subgroup. In this case, since four observations are in the subgroup, $D_4 = 2.28$ (see Table 6-3).

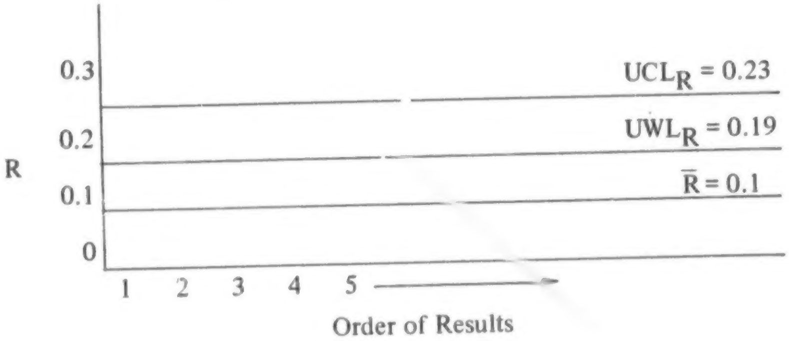
$$UCL_R = 2.28\ \overline{R} = 0.23$$

d. Calculate the Upper Warning Limit (UWL) on the range according to the formula:

$$UWL_R = 2/3\ (D_4\overline{R}\text{-}\overline{R}) + \overline{R}$$

$$UWL_R = 2/3\ [2.28\ (0.1)\text{-}0.1] + 0.1 = 0.19$$

e. Now graph $\overline{R}$, UWL_R, and UCL_R in the following manner:



f. Turning now to the $\overline{X}$ values, calculate the $UCL_{\overline{X}}$ by the formula:

$$UCL_{\overline{X}} = A_2\overline{R}$$

where A_2 is a constant dependent on the number of units in the subgroup. In this case, since four observations are in the subgroup, $A_2 = 0.73$ (see Table 6-3).

$$\therefore\ UCL_{\overline{X}} = 0.73\overline{R} = 0.07$$

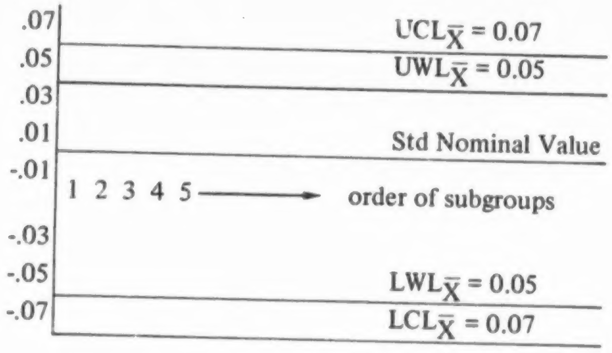
g. Calculate the $UWL_{\bar{X}}$ by the formula:

$$UWL_{\bar{X}} = 2/3\ A_2(\bar{R})$$

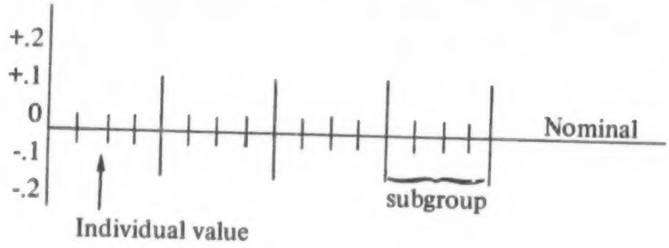
$$UWL_{\bar{X}} = 2/3\,[\,0.73\ (0.1)] = 0.05$$

Note: Lower Warning Limit ($LWL_{\bar{X}}$) and Lower Control Limit ($LCL_{\bar{X}}$) are simply the negative values of $UWL_{\bar{X}}$ and $UCL_{\bar{X}}$, respectively.

h. Now graph the standard Nominal Value (set equal to zero), $UWL_{\bar{X}}$, and $UCL_{\bar{X}}$, $LWL_{\bar{X}}$, and $LCL_{\bar{X}}$ in the following manner:



i. In order to detail any trends forming within each subgroup, individual differences may be plotted by preparing the following graph:



j. Thus, as in the precision control charts, once all of the above accuracy control charts have been constructed, all future data can be plotted on each set of duplicate spiked samples or standards, to determine if the system is in control, out of control, and/or to detect any trends developing within the system.

6.5 References

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CHAPTER 7

DATA HANDLING AND REPORTING

7.1 Introduction

To obtain meaningful data on water quality, the laboratory must first collect a representative sample and deliver it unchanged for analysis. The analyst must then complete the proper analysis in the prescribed fashion. Having accomplished these steps, one other important step must be completed before the data are of use. This step includes the permanent recording of the analytical data in meaningful, exact terms, and reporting it in proper form to some storage facility for future interpretation and use.

The brief sections that follow discuss the data value itself, recording and reporting the value in the proper way, means of quality control of data, and storage and retrieval.

7.2 The Analytical Value

7.2.1 Significant Figures

The term significant figure is used rather loosely to describe some judgment of the number of reportable digits in a result. Often the judgment is not soundly based and meaningful digits are lost or meaningless digits are accepted.

Proper use of significant figures gives an indication of the reliability of the analytical method used. The following definitions and rules are suggested for retention of significant figures:

A number is an expression of quantity. A figure or digit is any of the characters 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, which, alone or in combination, serves to express a number. A significant figure is a digit that denotes the amount of the quantity in the place in which it stands.

Reported values should contain only significant figures. A value is made up of significant figures when it contains all digits known to be true and one last digit in doubt. For example, if a value is reported as 18.8 mg/l, the "18" must be firm values while the "0.8" is somewhat uncertain and may be "7" or "9".

The number zero may or may not be a significant figure:

a. Final zeros after a decimal point are always significant figures. For example, 9.8 grams to the nearest mg is reported as 9.800 grams.

b. Zeros before a decimal point with other preceding digits are significant. With no other preceding digit, a zero before the decimal point is not significant.

c. If there are no digits preceding a decimal point, the zeros after the decimal point but preceding other digits are not significant. These zeros only indicate the position of the decimal point.

d. Final zeros in a whole number may or may not be significant. In a conductivity measurement of 1000 μmhos/cm, there is no implication that the conductivity is 1000 ± 1 μmho. Rather, the zeros only indicate the magnitude of the number.

A good measure of the significance of one or more zeros before or after another digit is to determine whether the zeros can be dropped by expressing the number in exponential form. If they can, the zeros are not significant. For example, no zeros can be dropped when expressing a weight of 100.08 grams in exponential form; therefore the zeros are significant. However, a weight of 0.0008 grams can be expressed in exponential form as 8×10^{-4} grams, and the zeros are not significant. Significant figures reflect the limits of the particular method of analysis. It must be decided beforehand whether this number of significant digits is sufficient for interpretation purposes. If not, there is little that can be done within the limits of normal laboratory operations to improve these values. If more significant figures are needed, a further improvement in method or selection of another method will be required to produce an increase in significant figures.

Once the number of significant figures is established for a type of analysis, data resulting from such analyses are reduced according to set rules for rounding off.

7.2.2 Rounding Off Numbers

Rounding off of numbers is a necessary operation in all analytical areas. It is automatically applied by the limits of measurement of every instrument and all glassware. However, it is often applied in chemical calculations incorrectly by blind rule or prematurely, and in these instances, can seriously affect the final results. Rounding off should normally be applied only as follows:

7.2.2.1 Rounding-Off Rules

a. If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example: 11.443 is rounded off to 11.44.

b. If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example: 11.446 is rounded off to 11.45.

c. When the figure following those to be retained is 5, and there are no figures other than zeros beyond the 5, the figure is dropped, and the last place figure retained is increased by 1 if it is an odd number, or it is kept unchanged if an even number. As an example: 11.435 is rounded off to 11.44, while 11.425 is rounded off to 11.42.

7.2.2.2 Rounding Off Single Arithmetic Operations

a. Addition: When adding a series of numbers, the sum should be rounded off to the same numbers of decimal places as the addend with the smallest number of places. However, the operation is completed with all decimal places intact and rounding off is done afterward. As an example:

$$\begin{array}{l} 11.1 \\ 11.12 \\ \underline{11.13} \\ 33.35 \end{array}$$

The sum is rounded off to 33.4.

b. Subtraction: When subtracting one number from another, rounding off should be completed before the subtraction operation, to avoid invalidation of the whole operation.

c. Multiplication: When two numbers of unequal digits are to be multiplied, all digits are carried through the operation, then the product is rounded off to the number of significant digits of the less accurate number.

d. Division: When two numbers of unequal digits are to be divided, the division is carried out on the two numbers using all digits. Then the quotient is rounded off to the number of digits of the less accurate of the divisor or dividend.

e. Powers and Roots: When a number contains n significant digits, its root can be relied on for n digits, but its power can rarely be relied on for n digits.

7.2.2.3 Rounding Off the Results of a Series of Arithmetic Operations

The rules for rounding off are reasonable for simple calculations, however, when dealing with two nearly equal numbers, there is a danger of loss of all significance when applied to a series of computations which rely on a relatively small difference in two values. Examples are calculation of variance and standard deviation. The recommended procedure is to carry several extra figures through the calculation and then to round off the final answer to the proper number of significant figures.

7.2.3 Glossary of Terms

To clarify the meanings of reports and evaluations of data, the following terms are defined. They are derived in part from American Chemical Society and American Society for Quality Control usage (1, 2).

7.2.3.1 Accuracy Data

Measurements which relate to the difference between the average test results and the true result when the latter is known or assumed. The following measures apply:

> Bias is defined as error in a method which systematically distorts results. The term is used interchangeably with accuracy in that bias is a measure of inaccuracy.
>
> Relative error is the mean error of a series of test results as a percentage of the true result.

7.2.3.2 Average

In ordinary usage, the arithmetic mean. The arithmetic mean of a set on n values is the sum of the values divided by n.

7.2.3.3 Characteristic

A property that can serve to differentiate between items. The differentiation may be either quantitative (by variables), or qualitative (by attributes).

7.2.3.4 Error

The difference between an observed value and its true value.

7.2.3.5 Mean

The sum of a series of test results divided by the number in the series. Arithmetic mean is understood ($\bar{X}$).

7.2.3.6 Population

Same as Universe. (See subparagraph 7.2.3.13).

7.2.3.7 Precision

Degree of mutual agreement among individual measurements. Relative to a method of test, precision is the degree of mutual agreement among individual measurements made under prescribed, like conditions.

7.2.3.8 Precision Data

Measurements which relate to the variation among the test results themselves, i.e., the scatter or dispersion of a series of test results, without assumption of any prior information. The following measures apply:

a. Standard Deviation (σ). The square root of the variance.

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} X_i^2}{n} - \bar{X}^2}$$

b. Standard Deviation, estimate of universe (s).

$$s = \sqrt{\frac{\sum_{i=1}^{n} X_i^2 - \frac{\left(\sum_{i=1}^{n} X_i\right)^2}{n}}{n - 1}}$$

c. Coefficient of Variance (V). The ratio of the standard deviation (s) of a set of numbers, n, to their average, $\bar{X}$, expressed as a percentage:

$$V = \frac{S}{X}$$

d. Range. The difference between the largest and smallest values in a set.

e. 95% Confidence Limits. The interval within which one estimates a given population parameter to lie, 95% of the time.

7.2.3.9 Sample

A group of units, or portion of material, taken from a larger collection of units, or quantity of material, which serves to provide information that can be used as a basis for judging the quality of the larger quantity as a basis for action on the larger quantity or on the production process. Also used in the sense of a "sample of observations."

7.2.3.10 Series

A number of test results which possess common properties that identify them uniquely.

7.2.3.11 Skewness (k)

A measure of the lopsidedness or asymmetry of a frequency distribution defined by the expression:

$$\frac{(X_i - \overline{X})^3}{n\sigma^3}$$

This measure is a pure signed number. If the data are perfectly symmetrical, the skewness is zero. If k is negative, the long tail of the distribution is to the left. If k is positive, the long tail extends to the right.

7.2.3.12 Unit

An object on which a measurement or observation may be made.

7.2.3.13 Universe

The totality of the set of items, units, measurements, etc., real or conceptual, that is under consideration.

7.2.3.14 Variable

A term used to designate a method of testing, whereby units are measured to determine, and to record for each unit, the numerical magnitude of the characteristic under consideration. This involves reading a scale of some kind.

7.3 Report Forms

The analytical information reported should include the parameter, the details of the analysis such as burette readings, absorbance, wavelength, normalities of reagents, correction factors, blanks, and finally, the reported value.

To reduce errors in manipulation of numbers, a good general rule is to keep data transposition to an absolute minimum. If this were pursued, the ideal report form would include all preliminary information of the analysis, yet it would be possible to use the same form through to the final reporting of data into a computer or other storage device. However, the ideal report form is not usually in use. Rather, a variety of methods are used to record data. They are:

7.3.1 Loose Sheets

Reporting of data onto loose or ring-binder forms is an older, but much used means of recording data. It does allow easy addition of new sheets, removal of older data, or collection of specific data segments. However, the easy facility for addition or removal also permits easy loss or misplacement of sheets, mix-ups as to date sequence, and questionable status in formal display, or for presentation as evidence.

7.3.2 Bound Books

An improvement in data recording is use of bound books which force the sequence of data insertion. Modification beyond a simple lined book improves its effectiveness with little additional effort. Numbering of pages encourages use in sequence and aids also in referencing data, through a table of contents, according to time, type of analysis, kind of sample, analyst, etc.

Validation can be easily accomplished by requiring the analyst to date and sign each analysis on the day completed. This validation can be strengthened further by providing space for the laboratory supervisor to sign off as to the date and acceptability of the analysis.

A further development of the bound notebook is the commercially available version designed for research-type work. These note books are preprinted with book and page numbers and spaces for title of project, project number, analyst signature, witness signature and dates. Each report sheet has its detachable duplicate sheet which allows for up-to-date review by management without disruption of the book in the laboratory. The cost is about four times that of ordinary notebooks.

Use of bound notebooks is essentially limited to research and development work where an analysis is part of a relatively long project, and where the recording in the notebook is the prime disposition of the data until a status or final report is written.

7.3.3 Pre-Printed Report Forms

Most field laboratories or other installations doing repetitive analyses for many parameters day in and day oût, develop their own system of recording and tabulating laboratory data. This may include bound notebooks; but a vehicle for forwarding data is also required. In many instances, laboratory units tailor a form to fit a specific group of analyses, or to report a single type of analysis for series of samples, with as much information as possible preprinted to simplify use of the form. With loose-sheet multicopy forms (use of carbon or NCR paper) information can be forwarded daily, weekly, or on whatever schedule is necessary, while allowing retention of all data in the laboratory. Still, the most common record is an internal bench sheet, or bound book, for recording of all data in rough form. The bench sheet or book never leaves the laboratory but serves as the source of information for ail subsequent report forms (See Figure 7-1).

In most instances the supervisor and analyst wish to look at the data from a sample point in relation to other sample points on the river or lake. This review of data by the supervisor, prior to release, is a very important part of the laboratory's quality control program; however, it is not easily accomplished with bench sheets. For this purpose, a summary sheet can be prepared which compares a related group of analyses from a number of stations. An example is shown in Figure 7-2. Since the form contains all of the information necessary for

Figure 7-1. EXAMPLE OF BENCH SHEET

NL-C-88
(7-68)
Spectrographic Analyses Bench Data

Sample #____ Date__________ Source_______________ TDS________

________ ml. conc. to__________ ml. Factor _______________

	Test Count	Sec
1.		
2.		
3.		

	Count			Rerun Count			Av. Count	PPM In Conc. Sample	Less Than	(μ g/1)PPB Orig. Sample
1. Zn									☐	
2. Cd									☐	
3. As									☐	
4. B									☐	
5. P									☐	
6. Fe									☐	
7. Mo									☐	
8. Mn									☐	
9. Al									☐	
10. Be									☐	
11. Cu									☐	
12. Ag									☐	
13. Ni									☐	
14. Co									☐	
15. Pb									☐	
16. Cr									☐	
17. V									☐	
18. Ba									☐	
19. Sr									☐	

Figure 7-2. EXAMPLE OF SUMMARY REVIEW SHEET

Table 2. MINERALS ANALYSES OF ZONE B, OHIO RIVER SAMPLES, CONC., mg/1.

STATION	Storet Number	Date 1969	Alkalinity	Hardness	Chloride	Sulfate	Fluoride	SOLIDS		
								Total	Diss.	Susp.
Ohio at Ironton	200152									
Ohio at Greenup Dam	200001									
Ohio at Portsmouth	200139									
Scioto at Lucasville	381710									
Ohio at Maysville	200153									
Ohio at Meldahl Dam	383070									
Little Miami at Cincinnati	380090									
Ohio at Cincinnati	380037									
Licking at 12th Street	200523									
Ohio at Miami Fort	383072									
Ohio at Markland Dam	200521									
Kentucky at Dam I	200522									
Ohio at Madison	174304									
Great Miami at Eldean										
Great Miami at Sellars Road	383047									
Great Miami at Liberty-Fairfield Road	383015									
Great Miami at American Materials Bridge	383007									
Whitewater at Suspension										
Great Miami at Lawrenceburg (Lost Bridge)	383071									

reporting data it is used also to complete the data forms forwarded to the storage and retrieval system.

The forms used to report data to data storage systems require a clear identification of the sample point, the parameter code, the type of analysis used, and the reporting terminology. Failure to provide the correct information can result in rejection of the data, or insertion in an incorrect parameter. As a group of analyses is completed on one or more samples, the values are reported in floating decimal form, along with the code numbers, for identifying the parameter and the sampling point (station). Figure 7-3 shows an example of a preprinted report form for forwarding data to keypunch.

7.3.4 Digital Read-out

Instrumental analyses, including automated, wet-chemistry instruments, such as Technicon AutoAnalyzer, atomic absorption spectrophotometer, pH meter, selective electrode meter, etc., now can provide direct digital readout of concentration, which can be recorded directly onto report sheets without further calculation. Electronics manufacturers now produce computer-calculators that will construct best-fit curves, integrate curves, and/or perform a pre-set series of calculations required to obtain the final reported value for recording by the analyst.

7.3.5 Key Punch Cards and Paper Tape

Since much of the analytical data generated in laboratories is recorded on bench sheets, transferred to data report forms, key-punched, then manipulated on small terminal computers, or manipulated and stored in a larger data storage system, there is a built-in danger of transfer error. This increases with each transposition of data. It is suggested that the analyst can reduce this error by recording data onto punch cards directly from bench sheets. The cards can be retained, or forwarded immediately to the data storage system as desired. IBM now offers a small hand-operated key-punch for this purpose.

It is anticipated that in future water quality systems, the intermediate report sheets will be eliminated and the data will be punched automatically by the analytical instrument system onto key-punch cards and/or paper tapes for direct use as computer input.

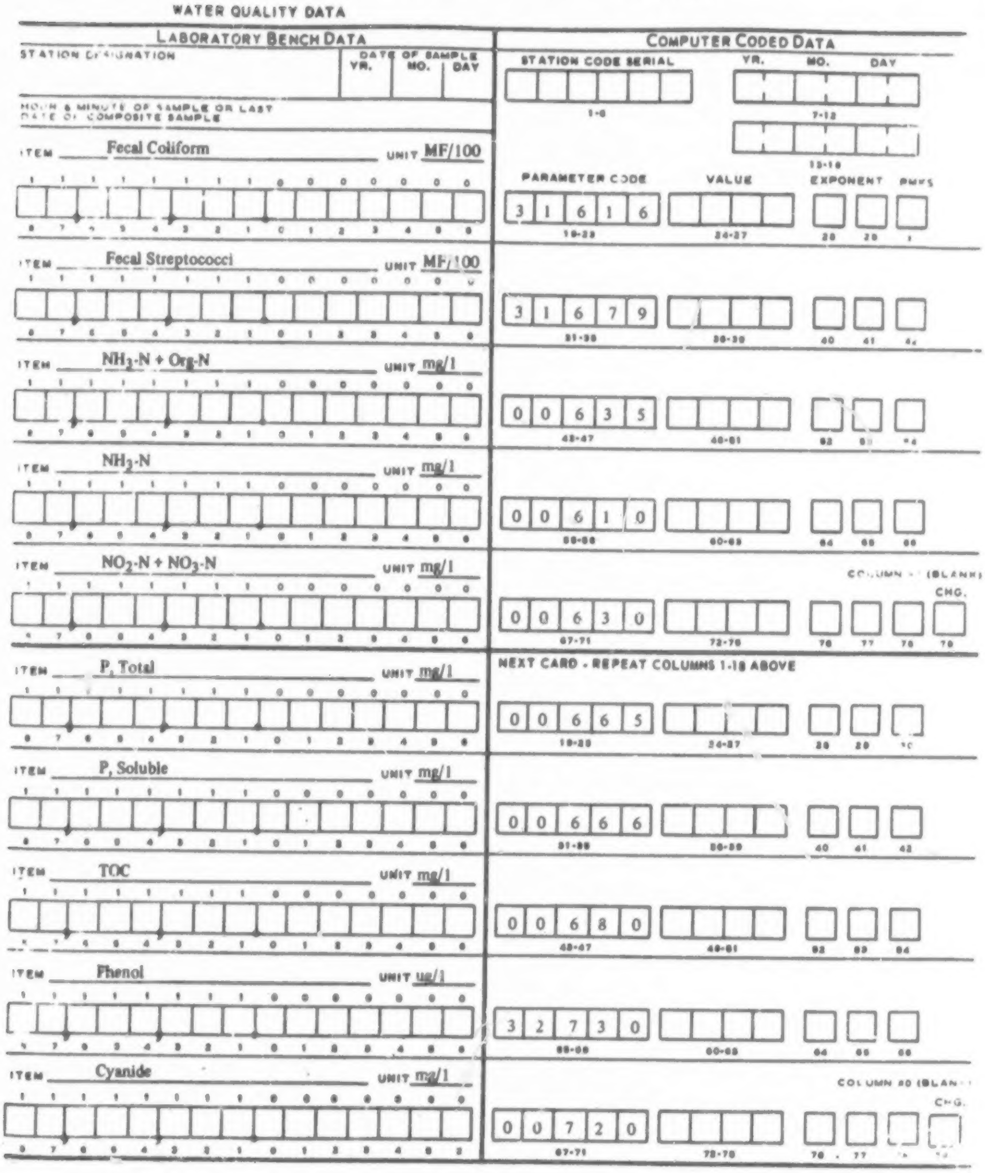
7.4 STORET–Computerized Storage and Retrieval of Water Quality Data

The use of computers with their almost unlimited ability to record, store, retrieve, and manipulate huge amounts of data is a natural outgrowth of demands for meaningful interpretation of the great masses of data generated in almost any technical activity.

In August 1961, an informal conference was held in the Basic Data Branch, Division of Water Supply and Pollution Control, U.S. Public Health Service. A number of ideas were brought together in the basic design of a system for storage and retrieval of data for water pollution control, called STORET. In 1966, the STORET system was transferred, with the Division, into the Federal Water Pollution Control Administration, U.S. Department of the Interior. A refinement of this system is now operated by the Technical Data and Information Branch, Division of Applied Technology, EPA.

If properly stored, the data can be retrieved according to the point of sampling, the date, the specific parameters stored, etc., or all data at a sample point or series of points can be

Figure 7-3. EXAMPLE OF STORET REPORT FORM



WATER QUALITY DATA

LABORATORY BENCH DATA

STATION DESIGNATION

DATE OF SAMPLE: YR. | MO. | DAY

HOUR & MINUTE OF SAMPLE OR LAST DATE OF COMPOSITE SAMPLE

COMPUTER CODED DATA

STATION CODE SERIAL (1-6) YR. MO. DAY (7-12)

(13-18)

Scale above boxes: 1 1 1 1 1 1 1 1 0 0 0 0 0 0 0

Scale below boxes: 8 7 6 5 4 3 2 1 0 1 2 3 4 5 6

ITEM	UNIT	PARAMETER CODE		VALUE	EXPONENT		RMKS	CHG.
Fecal Coliform	MF/100	31616	19-23	24-27	28	29	30	
Fecal Streptococci	MF/100	31679	31-35	36-39	40	41	42	
NH_3-N + Org-N	mg/l	00635	43-47	48-51	52	53	54	
NH_3-N	mg/l	00610	55-59	60-63	64	65	66	
NO_2-N + NO_3-N	mg/l	00630	67-71	72-75	76	77	78	79

COLUMN 80 (BLANK)

NEXT CARD - REPEAT COLUMNS 1-18 ABOVE

ITEM	UNIT	PARAMETER CODE		VALUE	EXPONENT		RMKS	CHG.
P, Total	mg/l	00665	19-23	24-27	28	29	30	
P, Soluble	mg/l	00666	31-35	36-39	40	41	42	
TOC	mg/l	00680	43-47	48-51	52	53	54	
Phenol	ug/l	32730	55-59	60-63	64	65	66	
Cyanide	mg/l	00720	67-71	72-75	76	77	78	79

COLUMN 80 (BLANK)

extracted as a unit.

There is a State/Federal cooperative activity which provides State water pollution control agencies with direct, rapid access into a central computer system for the storage, retrieval, and analysis of water quality control information.

Full details on use of the STORET system are given in the STORET handbook recently revised (3).

7.4 SHAVES–A Consolidated Data Reporting and Evaluation System

Information systems have been developed to bridge the gap between the analyst and his raw data, and a complex data storage and control system. These systems include preprinted report forms, computerized verification, and evaluation of data and data storage. An example is the SHAVES system.

The term, SHAVES, is an acronym for "Sample Handling and Verification System," which originated at the Great Lakes-Illinois River Basin Comprehensive Project Laboratory at Grosse Isle, Michigan. Although the system's original purpose was verification of the calculations following laboratory analyses, it now includes data storage, checks for completeness and consistency of data, procedures for submitting analytical requests, a set of forms for recording sampling and analytical information, and a clerical procedure to account for analyses completed and pending. The primary purposes of SHAVES are the standardization, automation and control of reporting analyses. All samples received at the Pacific Northwest Water Laboratory for routine analysis are processed through the system.

Although SHAVES uses a computer to perform its operations, it is not primarily a computer program. It is intended for use as an intra-laboratory quality control tool, and as such compliments the STORET system. It is described in detail elsewhere (4).

7.6 References

1. "Guide for Measure of Precision and Accuracy," Anal. Chem., Vol. 33, p. 480, (1961). p. 480.

2. "Glossary of General Terms Used in Quality Control," Quality Progress, Standard Group of the Standards Committee, ASQC, II, (7), pp. 21-2, (1969).

3. Water Quality Control Information System (STORET), EPA, Washington, D.C. 20460, Nov. 15, 1971.

4. Byram, K. V. and Krawczyk, D. F., "An Evaluation of SHAVES: A Water Quality Sample Handling System," Environmental Protection Agency, Pacific Northwest Water Laboratory, 1969.

CHAPTER 8

SPECIAL REQUIREMENTS FOR TRACE ORGANIC ANALYSIS

8.1 Introduction

The high sensitivity of the instrumentation used in trace organic chemical analysis, and the low concentration of compounds being investigated, dictate that special attention be given this field of analytical endeavor. Contamination of the sample from any possible source must be diligently guarded against, and interferences in the sample must be carefully controlled. Finally, strict attention to method and highly refined technique are required to produce valid quantitative results.

8.2 Discrete Bottled Samples

Sample collection should be done with wide-mouth glass bottles, equipped with screw caps fitted with Teflon liners. The use of a screw cap without a Teflon liner may cause contamination of the sample by the liner or adhesive used in sealing the liner to the cap. Plastic bottles (polyethylene) are not used because traces of plasticizer may be leached from the plastic by the water, and can be a source of analytical interference. Moreover, organics from the sample may be adsorbed on the plastic. It has been suggested that high grade Teflon bottles may be satisfactory for this use; however, the cost is prohibitive at present. Many investigators avoid the use of glass sample bottles, because breakage in shipment frequently causes loss of sample. This is overcome by the use of relatively inexpensive, expanded polystyrene foam shipping containers molded to fit the bottle. These shipping containers can be purchased from Preferred Plastics Corp., North Grosvenordale, Connecticut.

To insure freedom from organic contaminants, bottles are rinsed successively with chromate cleaning solution, running tap water, distilled water, and finally several times with redistilled solvent (e.g., acetone, hexane, petroleum ether, chloroform). Caps are washed with detergent, rinsed with tap water, distilled water, and solvent. Liners are treated in the same way as the bottles and are stored in a sealed container.

Each method designates a recommended sample size for surface water analysis. Duplicate samples are recommended. If analysis by more than one method is to be requested on the same sample, sufficient sample must be simultaneously obtained to supply the needs of each analysis.

It is also recommended that when requesting a non-specific analysis, any information that could help direct the analytical approach, or aid in interpretation of results, be supplied. Such information could include industrial or agricultural activities in the area from which the sample was obtained, spills, or other accidents that may have occurred in the area. Also mention of similar upstream activity could provide valuable assistance.

Samples should be stored in a cool, dark place, and analyzed as soon as possible. If the sample cannot be analyzed immediately, reporting the holding time can help in interpreting results where die-off rates are known.

8.3 Carbon Adsorption Samples

The affinity of carbon for organic substances requires that supplies of carbon be protected from extraneous sources of contamination. For example, carbon can adsorb organic substances such as paint vehicles and insecticides from the air. Therefore, the carbon is stored and processed in an area adequately protected from such sources of contamination. As an additional precaution, the ventilating, heating, and air-conditioning systems for the laboratories in which carbon adsorption samples are processed are completely isolated from all other laboratories. All carbon is obtained from the manufacturer in sealed metal drums. Obviously, spraying with pest-control chemicals is not permitted in these areas. Carbon blank determinations supplement these precautions.

8.4 Glassware

Proper calibration of volumetric glassware is essential to valid analytical results, because quantitation is performed by comparison to measured amounts of standard compounds, and by accurate measurement of sample volume.

Individual concentrator tubes, used to measure final concentrate volumes, must first be calibrated at the working volume. This is particularly important for volumes less than 1 ml. Calibration should be made by noting the number of microliters of solvent required to bring the liquid level (lower miniscus) up to a particular graduation mark. A precision 100 μl syringe should be used to measure calibration volume.

It is also very important in trace organic analysis that glassware be as free as possible of any organic contaminants. A chromic acid cleaning solution is required for removing all traces of organic material from glassware.

8.5 Reagents and Chemicals

The minimum purity of reagents and chemicals should be analytical reagent grade. Analytical standards should be reference grade, when available. The analyst should take special note of the assay of less pure materials (most often pesticides). All reagents and chemicals should be stored according to manufacturer's instructions to prevent degradation. Proper storage is especially important if the chemical is to be used in preparing an analytical standard. Refrigerated chemicals should be allowed to come to room temperature before exposing them to the atmosphere.

When preparing stock solutions, it is recommended that at least 0.100 gram of material be used for greater accuracy in weighing. Solutions should be carefully stored so as to preserve their concentration, and to protect them from ultraviolet radiation. Usually storage in ground-glass stoppered bottles, either amber-colored, or out of the line of direct lighting, is sufficient.

Standard solutions should be prepared using precision syringes, preferably equipped with a Cheney adapter, to measure the volume of stock solution to be diluted. The syringe barrel should be pre-wetted with solvent and air bubbles expelled. Dilution should be done in a Class A volumetric flask to insure accurate measurement. If these solutions are to be used frequently, they are best stored in a screw-cap, septum, sealed vial. These vials allow instant access to the solution and offer good protection against concentration changes of the standard solution. Evaporation of the solvent caused by repeated removal of the cap is a serious problem with other containers. If septum vials are not available it is advisable to prepare standard solutions in a volumetric container of 100 ml or more and transfer a small portion to a separate container for daily use, then discard that portion at the end of the day.

All stock or standard solutions should be carefully watched for signs of changes in concentration or deterioration. As an aid to monitoring these solutions, it is wise to label them as to compound, concentration, solvent used, date, and preparer. Also, in the case of GC solutions, it is necessary to retain some evidence of its chromatographic behavior as a fresh solution for comparison at a later date.

Distilled water used as dosed, control samples must be free of organic interferences. A very effective way of removing organic interferences from distilled water is to pre-extract the water with the solvent that is to be used in the analysis, then boil the water to remove the residual solvent.

Organic solvents used in pesticide analysis should be pesticide quality, and demonstrated to be free of interferences in a manner compatible with whatever analytical operation is to be performed. Solvents can be checked by analyzing a volume equivalent to that used in the analysis and concentrated to the minimum final volume. Possible interferences are noted in terms of factors such as relative retention times, peak geometry, peak intensity, and width of solvent response. Interferences noted under these conditions can be considered maximum. If necessary, a solvent must be redistilled in glass using a 60-cm column packed with 1/8" glass helices, or an equivalent system.

Hexane - ethyl ether and benzene are commonly used in the extraction of water and wastewater in conjunction with analysis by electron-capture gas-liquid chromatography. Because electron-capture detection methods are extremely sensitive to interferences normally found in these solvents, the cleanest possible reagent grade or pesticide-quality solvents must be used. Redistillation in the lab in an all-glass system is usually necessary. Experience in the Analytical Quality Control Laboratory has shown Burdick-Jackson hexane and Baker Chemical Co. ethyl ether to be satisfactory. All solvents vary from lot to lot. Therefore, when a good lot is found, subsequent order should specify that lot number. Solvents in the same lot may also vary and therefore each container should be checked.

8.6 Common Analytical Operations

Adequate steps must be taken to eliminate or minimize interferences from solvents and other materials. A blank should be run simultaneously under the same analytical conditions as any block of samples analyzed. A block of samples is defined as any group of one or more samples analyzed using a common batch of analytical supplies. Should any one of the supplies be changed (i.e. solvent, silica gel, Florisil, etc.) a new blank is required.

Quantitation of micro amounts of organic materials requires extremely careful technique to avoid loss of sample. Quantitative transfers are essential to obtain accurate and precise results. Practice in these manipulations is recommended for the inexperienced analyst.

Concentration of sample extracts to very small volumes for micro analysis requires great care to avoid loss of constituents. A Kuderna-Danish evaporator is a very useful apparatus to accomplish this operation. Instructions in the use of this evaporator must be strictly followed to avoid loss of desired sample (1). Final concentration in an ampule or calibrated tube is accomplished in a warm water bath with a gentle stream of clean, dry air, if air oxidation is not a problem; otherwise, nitrogen should be used. During the final concentration, the inside walls should be rinsed repeatedly with the working solvent to insure the total sample is contained in the bottom of the tube. Complete evaporation of solvent must be avoided to prevent loss of sample constituents. The step should be accomplished within 10 or 12 minutes for best results.

8.7 Gas-Liquid Chromatography

To obtain reproducible results, it is necessary to have very accurate control of the column oven temperature. The temperature should be reproducible within ± 1°C, and have minimum gradients of 2°C throughout the oven. For temperature-programmed operation, a low mass oven is required to allow rapid heating and cooling of the column. Most manufacturers produce gas chromatographs which meet these requirements. Many organic compounds decompose when they come in contact with hot stainless steel. For this reason the injection block should be capable of accepting a quartz or glass tube to prevent the compounds from contacting hot metal. Memory peaks observed using direct, aqueous-injection, gas chromatography can be eliminated or greatly reduced by employing direct on-column injection. A Bio-med injection kit manufactured by Tracor Instrument Co. is very suitable for this purpose.

The septum should be changed at the end of each day's use. Changing at the end of each day allows overnight purging of the system of any bleed-off of contaminants from the septum. To avoid most of this bleed-off the septa can be preconditioned by heating at 250°C in a vacuum oven for two hours.

The gas chromatograph should be equipped with accurate needle-valve, gas-flow controls. If these flow controls are not previously calibrated this can easily be done using a soap-bubble flow meter and a stopwatch.

The nature of constituents to be measured dictates the type of detector to be employed. The electron capture detector is extremely sensitive to electronegative functional groups and substituents, such as: halogens, conjugated carbonyls, nitrites, nitrates, and organometals. It is virtually insensitive to hydrocarbons, alcohols, and ketones. The selective sensitivity to halides makes this detector particularly valuable for the analysis of many pesticides.

Electron capture detectors employing two sources of ionization are available: tritium (H^3) and radioactive nickel (Ni^{63}). Each has its advantages. Most H^3 detectors possess greater sensitivity than Ni^{63} detectors. However, the H^3 detector is limited to 225°C because of radioactive leakage. This temperature limitation makes the H^3 detector susceptible to a buildup of high-boiling contaminants which reduce its sensitivity. The Ni^{63} detector can be operated up to 400°C to prevent this buildup of contamination.

The microcoulometric detector is specific for halogen-, sulfur-, or nitrogen-containing compounds depending on the conditions used. Although the sensitivity of this detection system is not as great as others available, the extreme specificity makes it a very valuable device in indentification, minimizing the need for cleanup of the extract.

Another selective detector, with about the same sensitivity for chlorinated compounds as microcoulometric titration, is the Coulson electrolytic conductivity detector. The specificity of this detector makes it very useful in the identification of pesticides, and sample cleanup and pre-treatment are less critical. However, if chlorinated compounds are being detected, a scrubber tube must be used with this instrument to remove any SO_2 produced by sulfur-containing compounds in the sample.

The flame ionization detector (FID) responds to virtually all compounds. Some notable exceptions are air, water, carbon disulfide, and the fixed gases. This makes the FID very useful for direct- aqueous-injection gas chromatography. However, since the detector is sensitive to such a wide range of compounds, it is also subject to interference from extraneous material. This means that the extract must be cleaned up considerably before analysis. The flame photometric detector (FPD) is used to analyze residues of phosphorus- and sulfur-containing pesticides and their metabolities. Little or no cleanup of the sample extract is required, and extraneous material causes no appreciable interference.

The alkali flame detector (Thermionic) can also be used in the analysis of organophosphate pesticides. Even though this detector gives an enhanced response to phosphorus, a large amount of extraneous material demands that the extract be cleaned up before the phosphorus-containing constituents are quantitated. An enhanced response to sulfur is not obtained with the alkali flame.

A one-millivolt, one-second, full-scale-response, strip-chart recorder should be used to maintain a permanent record of the results.

The type of detector employed dictates the type of carrier gas that must be used. Nitrogen can be used for the FID, electron-capture, flame-photometric, and microcoulometric titration detectors. The Analytical Quality Control Laboratory has used nitrogen from various suppliers, and has found the J. T. Baker Chemical Company's extra dry grade to be satisfactory. However, to avoid the risk of system or detector contamination from materials possibly present in the gas cylinder, the cylinder should be replaced when the tank pressure reaches 200 psi. It is also recommended that some type of gas purifier which is composed of a molecular sieve, desiccant, and filter be used on all combustion gases and carrier gases used with electron capture detectors.

A precision, gas-tight, microliter syringe, which can be accurately filled, will deliver reproducible injections, and can be easily and thoroughly cleaned, is recommended for gas chromatographic use. A Teflon plunger seal to prevent backwash, and no dead volume are desirable features. These types of syringes are available from various suppliers, but the Glencoe syringes have additional design features to prevent bending plungers.

It is not possible to enumerate here the many types and applications of liquid phases and solid supports. The literature (2, 3) will provide helpful guidance in the selection of these materials.

The type of column tubing required to perform a specific GC analysis is prescribed by the method for that analysis. Aluminum has been found suitable for chlorinated organic pesticides and stainless steel for phenols. Generally 1/8" or 1/4" OD tubing is used. The 1/4" column is capable of accepting larger injections but the 1/8" column is more efficient at chromatographing small injections. It should be noted that the use of glass columns will prevent the degradation of material often associated with metal columns.

Silanized glass wool should be used to minimize degradation or absorption of organic compounds by the glass-wool plugs. Glass wool can be silanized by treating with 10%

dimethyldichlorosilane in toluene for 10 minutes, or the prepared material can be purchased from Applied Science Laboratories.

Column packings can be prepared by the analyst, or purchased already prepared and conditioned. If prepared in the laboratory a highly refined technique should be developed by the analyst. A well prepared packing is essential to an acceptable chromatographic analysis. Particular care should be taken to accurately measure loadings, uniformly distribute the liquid phase, and preserve the structure of the fragile solid support. One method used successfully is the beaker slurry method in which the proper amounts of stationary phase and solid support are mixed together in a solvent in a beaker. The solvent can be evaporated by immersing the beaker in a warm water bath or filtering it through a Buchner funnel. The mixture is then dried at 110°C to remove residual solvent. A fluidized dryer (4) may also be used to remove the remaining solvent. Details on techniques for preparation of Teflon packings may be obtained from Applied Science Laboratories (Bulletin FF124).

An important consideration in packing a column is obtaining a uniform density, not so compact as to restrict gas flow, and not so loose as to create voids during use. Also important is the need to exercise care not to crush particles during packing.

It cannot be overemphasized that column conditioning is essential to obtain acceptable GC analysis. Proper conditioning further distributes the liquid phase over available active sites, and removes excess liquid phase that may bleed off the column and impair GC performance. Unstable performance in the form of baseline drift, varying sensitivity, and wide solvent peaks are usually the result of column bleed due to improper conditioning. This also contaminates the detector and makes frequent cleaning necessary.

A good general procedure for conditioning columns is as follows: install the column, leaving it disconnected from the detector; heat the column in the GC oven to just above maximum recommended operating temperature for the liquid phase, without gas flow, for 2 hours; follow with a half-hour equilibration period at a temperature at least 40 degrees below the maximum recommended temperature, still without flow; raise the temperature 20 degrees above operating conditions (do not exceed the maximum recommended operating temperature for the liquid phase), adjust gas flow to 50 ml/min, and maintain these conditions 24 to 48 hours.

There are many factors that must be considered in any attempt to obtain optimum operating conditions. As indicated, optimum conditions begin with the proper selection of column materials including tubing, glass wool, liquid phase, and solid support. Each method dictates the selection of these items including the percent liquid phase. Liquid load and operating temperature are critical to optimum resolution and elution rate. Uniformly coating the solid support, properly packing the column, and properly conditioning the column all contribute greatly to attaining optimum conditions. Improper attention to these factors contributes to either column bleed, which fouls the detector, or tailing peaks, which prevent resolution of closely eluting compounds.

The system must be free of gas leaks since these affect sensitivity and reproducibility. The proper selection of a carrier gas is important. Injection blocks should be of proper flow design, and should be kept clean. Temperature control of injection port, column oven, and detector must be accurate and constant, and must be at equilibrium to obtain reproducible results.

Considerable attention must be given to those factors affecting detector response, such as gas flows and regulated current. Also, standard solutions and condition of electrodes for MCT detectors, condition of radioactive source for EC detectors, and ratio of combustion gases in flame ionization detectors must be carefully attended to.

The gas chromatograph must either be operated within the linear range of the detector, or a suitable calibration curve must be employed. The linear range can be determined by chromatographing different amounts of a compound and observing the response. The peak area of the responses should be proportional to the amount of compound injected throughout the full range of the recorder. If these conditions are not fulfilled at the attenuation investigated, a more sensitive attenuation should be selected until the linear range is found.

Once having obtained optimum operating conditions, the analyst must assure sustained optimum performance through a routine maintenance program, as prescribed in the instrument manual. Such common practices as inspecting for gas leaks, changing the septum after daily use, replacing gas tanks before they run too low, and keeping a close check on injection block, oven, and detector temperatures must be performed frequently.

Column performance can be monitored by observing daily response to a selected group standard, and comparing it to response to that same standard under previously determined optimum conditions. Changes in elution pattern, relative proportions of peaks, and peak geometry are signs of a deteriorating column if the rest of the system has been properly maintained. A column should be replaced as soon as deterioration is observed.

A good syringe-handling technique is important when doing GC analysis. Before measuring the volume to be injected into the gas chromatograph, first wet the barrel of the syringe and expel all air bubbles. The volume injected is determined by drawing a selected portion of the extract entirely into the glass, calibrated, syringe barrel, noting the volume, injecting the sample, partially withdrawing the plunger, and measuring the liquid remaining in the syringe barrel. Injections are made rapidly after the needle is in the gas chromatographic injection port. The needle is immediately removed from the system to prevent volatilization of any sample in the needle. This method improves the analytical accuracy since any absolute volume is injected and reproducible technique is not required. It also eliminates the built-in bias of injecting slightly more than expected each time, when direct barrel readings are used exclusively.

The standard solutions can be more accurately used if prepared at a concentration that allows injection volumes similar to those of the sample.

8.8 Qualitative Analysis

The retention time (R_t) of a component on a given column, under given conditions, is characteristic of that particular component, and is used for qualitative identification. The standard way of reporting retention data is to give the relative retention (RR_t) defined as R_t (component) ÷ R_t (reference compound). The retention time may be measured as the time elapsed from an unrestrained solute peak elution, to the apogee of the peak of interest. This works well when a flame ionization or electron-capture detector are used. However, when the microcoulometric titration or the flame photometric detector are used (the flame is extinguished by the injection), no unrestrained solute peak is observed. In such cases, the injection point is manually or electrically marked, and used as the point of reference for retention times. Caution must be exercised when manual marking is practiced, so that an accurate reference point is provided.

Tentative identification is made by matching the relative retention time of the unknown component with that obtained from a known compound analyzed under identical conditions, provided that peak geometry is also similar. It must be pointed out that similarity of retention time and peak geometry to a known compound does not unequivocally identify an unknown. Additional gas chromatographic columns of different polarity and other detectors may be used for confirmation. If retention time and peak geometry match on two or more columns, the identity is corroborated. However, further corroboration using analytical tools such as infrared spectroscopy, mass spectrometry, or thin-layer chromatography should be used whenever possible.

Proof of identity of compounds which produce a multi-peak response should be evidenced, not only by relative retention and peak geometry, but also by the correct number and relative proportion of each peak in the total chromatogram. This is called a "fingerprint" comparison of the known standard chromatogram with that of the unknown constituent.

8.9 Quantitative Analysis

The quantitative interpretation of a gas chromatogram is based either on the peak height or the peak area. The area measurement is generally preferred because peak height is extremely sensitive to small changes in the operating conditions, particularly in the column temperature. However, in chromatograms where the peaks are extremely sharp and narrow, the error involved in the area measurement makes height measurements more reliable.

Peak area measurement should be carried out using height x width at half height, disc integrator, or electronic digital integrator. These techniques are rapid and simple, and give good results with symmetric peaks of reasonable width. The use of a planimeter, although less precise than other methods, is presently found to be the best method for measuring the area of unsymmetric peaks which do not originate at the baseline. Precision is improved by tracing each peak several times and taking an average value. The electronic integrator is also recommended for those unsymmetric peaks which originate at the original baseline.

Concentrations of constituents are determined from standard calibration curves obtained under identical conditions. An absolute calibration curve is obtained from peak areas or peak heights plotted against known weights of a compound chromatographed under identical conditions. These standard injections must be made during the sample run to detect any change in instrument conditions or response which would invalidate the calibration.

The use of an internal standard is the most accurate method of quantitating constituents in a sample. A calibration curve can be obtained by simultaneously chromatographing the previously identified sample constituent and a standard, in known weight ratios, and plotting the weight ratios versus area ratios. An accurately known amount of the standard is then added to the unknown sample and the mixture chromatographed. The area ratios are calculated, and the weight ratio of the sample constituent to the standard is read from the curve. Since the amount of standard added is known, the amount of the sample constituent can be calculated. Using this method, injection volumes need not be accurately measured and detector response need not remain constant since any change in response will not alter the ratio.

If the following requirements can be met, the internal standard is the preferred method of calibration. The internal standard must be well resolved from other peaks, must elute close to peaks of interest, should approximate the concentration of unknown, and should have structural similarity to unknown.

8.10 Thin-Layer Chromatography

Special equipment for thin-layer chromatography as supplied by the Brinkman Instrument Company has been found by the Analytical Quality Control Laboratory to be particularly convenient to use. Adsorbents supplied by Warner-Chilcott Laboratories, particularly Silica Gel G and Alumina G, are found to be free of impurities. In any case, it is best to check the adsorbent for impurities, and discard it if necessary. Plates precoated by the manufacturer can often be used when quantitation is visual; however, trials of plastic-backed plates in the Analytical Quality Control Laboratory have shown that they often develop unevenly and very slowly. The use of precoated glass-backed plates is therefore recommended.

Prepared plates should be carefully inspected for flaws that might interfere with proper chromatographic development. Plates should be marked in such a way that any grain lines would be perpendicular to the direction of development when used. Prepared plates are best activated by heating at 110°C in a convection oven for 30 minutes. Phosphorous pentoxide is recommended as the desiccant for use when storing plates.

Two important points to remember before using the developing chambers are to give the chamber atmosphere time to become saturated with solvent vapor, and to keep the chamber in constant temperature surroundings shielded from drafts. Failure to observe these points could result in an erratic chromatographic development, generally off line.

When spotting a plate, care must be taken not to overload the spot. Overloading results in poor chromatographic efficiency. Also, when applying a gentle stream of air or other gas to evaporate the solvent, care must be taken not to blow away any of the layer or sample droplets. The analyst should also be aware of whether or not the use of air to evaporate the solvent could cause any oxidation of the sample material, thereby causing erroneous results. If oxidation is a problem an inert gas should be substituted.

When spraying a plate with aqueous or other non-volatile sprays, care should be taken not to soak the plate. Soaking with such sprays may cause spots to run as the plate stands vertically. When using any spray it is better to use a stronger solution, then apply increased amounts to develop the spots. Overspraying can produce a background color which impairs the visibility of the developed spot.

Quantitation by visual comparison of sample response to a series of standards is semi-quantitative at best. However, by making the spot size the same for samples and standards,by using the same solvent for both, and by using careful development techniques, a fair degree of reliability can be obtained, when comparing the factors of spot size and color intensity.

When zone scraping and collecting the layer material with the aid of a vacuum, the collection apparatus is usually plugged with glass wool to trap the adsorbent. Since poorly packed glass wool can cause high loss of material by failure to trap the dust, the scraping of the periphery of the zone should be done first. A clear tygon vacuum line, or a glass section near the end of the tube makes it easy to monitor for untrapped adsorbent.

8.11 Column Chromatography

The features of a chromatographic column which define its utility are shape, liquid capacity, and elution rate. The liquid capacity is principally a matter of convenience and should be weighed against the increased labor required for cleaning equipment. A flow-control device is critical to an efficient separation because increased flow decreases resolution between emerging components. A Teflon, flow-control stopcock is required because lubricant will produce an analytical interference.

Most adsorbents used in column chromatography are preactivated by the manufacturer and shipped in air-tight containers. Storage in the laboratory should also be in an air-tight container because moisture will greatly affect the activation state of an adsorbent. If a second activation step is required, the material should be heated at 130°C for at least five hours. The activity of the adsorbent can be monitored by eluting a mixture of chromatographically pure dyes (5). The elution rate and degree of separation of the individual dyes is a function of the activation state of the adsorbent. This enables the analyst to accurately attain the same activation for different batches of adsorbent.

When the adsorbent is added to the column, gentle tapping or a vibrator should be used to settle the material. This minimizes the space between particles and prevents channeling of the eluting solvent through the adsorbent which reduces separation efficiency.

Liquids should be added slowly, down the inside wall of the column, to avoid disturbing the packing surface. Mixing of the solution above the adsorbent with the fresh eluting solvent can be minimized by introducing the new solvent just as the last of the solution reaches the packing surface. The column top must not go dry or air may be introduced which will lower the separation efficiency of the system.

Before addition of the sample, columns should be pre-eluted with 50-75 ml of the solvent prescribed by the procedure. This is done to remove trapped air and to clean the column material of trace contaminants. During this pre-elution it is often necessary to tap the column to free all trapped air, especially if a volatile solvent is used in the pre-elution.

8.12 References

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CHAPTER 9

SKILLS AND TRAINING

9.1 General

Analytical operations in the laboratory can be graded according to the degree of complexity. Some analyses require no sample treatment, with the measurement performed in minutes on a simple instrument. Other determinations require extensive sample preparation prior to complex instrumental examination. Consequently, work assignments in the laboratory should be clearly defined. Each analyst should be completely trained and fully understand all the assignments of his job before being given new responsibilities. In this regard, all analysts, sub-professional or professional, should be thoroughly instructed in basic laboratory operations, according to the degree of professional maturity. Some of the basic operations that should be reviewed periodically with laboratory personnel follow:

a. Sample Logging

Emphasize the routine procedure for recording of samples entering the laboratory, and assign primary responsibility. Establish what information is required, and how sample is routed to analyst. Discuss stability of samples, and how they should be stored prior to analysis.

b. Sample Handling

The analyst should understand thoroughly when the sample is to be settled, agitated, poured, pipetted, etc., before removal from the container.

c. Measuring

The analysts, especially new employees and sub-professionals, should be instructed in the use of volumetric glassware. The correct use of pipettes and graduates should be emphasized as discussed in Chapter 4.

d. Weighing

Because almost every measuring operation in the analytical laboratory is ultimately related to a weighing operation, the proper use of the analytical balance should be strongly emphasized. Maintenance of the balance, including periodic standardization, should be reiterated to all personnel.

e. Glassware

All glassware should be washed and rinsed following the requirements of the analysis to be performed. Not only must the personnel assigned to this task be instructed, but all lab personnel should know the routine for washing glassware, and also special requirements for particular uses. In addition, the precision tools of the laboratory such as pipets, burets, graduates, Nessler tubes, etc., should be inspected before use for cleanliness, broken delivery tips, and clarity of marking. Defective glassware should be discarded or segregated.

In summary, quality control begins with basic laboratory techniques. Individual operator error and laboratory error can be minimized if approved techniques are consistently practiced. To insure the continued use of good technique, laboratory supervisors should periodically review the basic techniques with each analyst and point out, when necessary, areas of needed improvement.

Continuing improvement of technical competence for all laboratory personnel is, of course, the final responsibility of the laboratory supervisor. In a well organized laboratory, however, a big brother attitude of higher ranking to lower grade personnel should be encouraged; each person should be eager to share experience, tricks-of-the-trade, special skills, and special knowledge with subordinates. Obviously, improved efficiency and improved data quality will result.

9.2 Skills

The cost of data production in the analytical laboratory is based largely upon two factors–the pay scale of the analyst, and the number of data units produced per unit of time. However, estimates of the number of measurements that can be made per unit of time are difficult, because of the variety of factors involved. If the analyst is pushed to produce data at a rate beyond his capabilities, unreliable results may be produced. On the other hand, the analyst should be under some compulsion to produce a minimum number of measurements per unit of time, lest the cost of data production become prohibitive. In the following table, estimates are given for the number of determinations that an analyst should be expected to perform on a routine basis. The degree of skill required for reliable performance is also indicated. The arbitrary rating numbers for the degree of skill required are footnoted in the tables, but are explained more fully below:

a. Rating 1–indicates an operation that can be performed by a semi-skilled sub-professional with limited background; comparable to GS-3 through GS-5.

b. Rating 2–operation requires an experienced aide (sub-professional) with background in general laboratory technique and some knowledge of chemistry, or a professional with modest training and experience; comparable to GS-4 through GS-7.

c. Rating 3–indicates a complex procedure requiring a good background in analytical techniques; comparable to GS-7 through GS-11.

d. Rating 4–a highly involved procedure requiring experience on complex instruments; determination requires specialization by analyst who interprets results; comparable to GS-9 through GS-13.

The time limits presented in the table are based on use of EPA methods.

A tacit assumption has been made that multiple analytical units are available for measurements requiring special equipment, as for cyanides, phenols, ammonia, nitrogen and COD. For some of the simple instrumental or simple volumetric measurements, it is assumed that other operations such as filtration, dilution or duplicate readings are required; in such cases the number of measurements performed per day may appear to be fewer than one would normally anticipate.

Table 9-1

SKILL-TIME RATING OF STANDARD ANALYTICAL OPERATIONS

Measurement	Skill Required (Rating No.)	No./Day
	(Simple Instrumental)	
pH	1	100-125
Conductivity	1	100-125
Turbidity (HACH 2100)	1	75-100
Color	1	60-75
DO (Probe)	1, 2	100-125
Fluoride (Probe)	1, 2	100-125
	(Simple Volumetric)	
Alkalinity (Potentiometric)	1	50-75
Acidity (Potentiometric)	1	50-75
Chloride	1	100-125
Hardness	1	100-125
DO (Winkler)	1, 2	75-100
	(Simple Gravimetric)	
Solids, Suspended	1, 2	20-25
Solids, Dissolved	1, 2	20-25
Solids, Total	1, 2	25-30
Solids, Volatile	1, 2	25-30
	(Simple Colorimetric)	
Nitrite N (Manual)	2	75-100
Nitrate N (Manual)	2	40-50
Sulfate (Turbidimetric)	2	100-125
Silica	2	100-125
Arsenic	2, 3	20-30

SKILL REQUIRED

1 - aide with minimum training, comparable to GS-3 through GS-5

2 - aide with special training or professional with minimum training, comparable to GS-5 through GS-7.

3 - experienced analyst, professional, comparable to GS-9 through GS-12.

Table 9-1 (continued)

SKILL-TIME RATING OF STANDARD ANALYTICAL OPERATIONS

Measurement	Skill Required (Rating No.)	No./Day
	(Complex, Volumetric or Colorimetric)	
BOD	2, 3	30-40*
COD	2, 3	25-30
TKN	2, 3	25-30
Phosphorus, Total	2, 3	50-60
Phenol (Dist'n only)	2, 3	20-30
Oil & Grease (Soxhlet)	2, 3	15-20
Fluoride (Dist'n)	2, 3	25-30
Cyanide	2, 3	10-15
	(Special Instrumental)	
Metals by AA (No preliminary treatment)	2, 3	150
Metals by AA (With preliminary treatment)	2, 3	60-80
Pesticides by GC (Without cleanup)	3, 4	3-5
Pesticides by GC (With cleanup)	3, 4	2-4

SKILL REQUIRED

2 - aide with special training or professional with minimum training, comparable to GS-5 through GS-7.

3 - experienced analyst, professional, comparable to GS-9 through GS-12.

4 - experienced analyst, professional, comparable to GS-11 through GS-13.

* - depends on type of sample.

9.3 Training

For more experienced, higher grade personnel, formal training in special fields, possibly leading to specialization, should be almost mandatory. Such training can be fostered through local institutions and through the training courses provided by the Environmental Protection Agency. Regional policies on after-hours, government-supported training should be properly publicized.

Formalized training for lower grade personnel, comparable to GS-3 to GS-5, is relatively scarce. However, skills can be most efficiently improved at the bench level on a personal, informal basis by more experienced analysts working in the same area. Exposure to pertinent literature should also be a definite program policy.

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